Science & Progress

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# A. Chemistry

# Novel gold(I) complexes decorated by phosphine and terpyridine ligands

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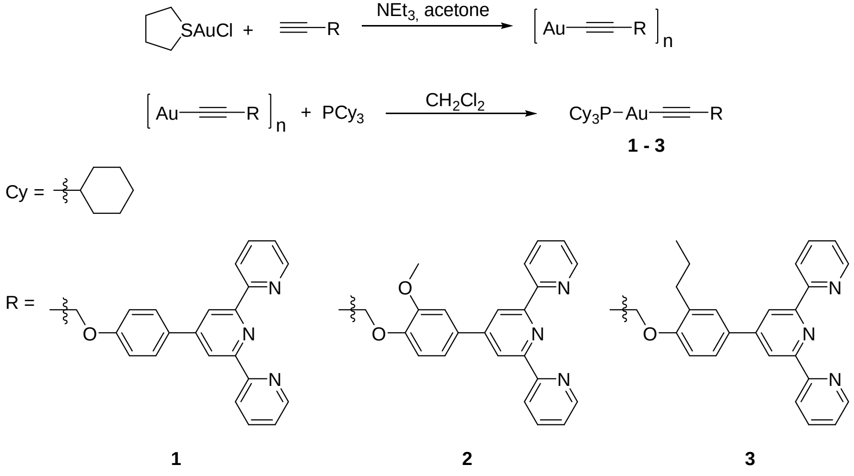
Nowadays, a molecule capable to detecting of cations are of great interest. Their feature is that they give a strong and stable luminescent response to different metal cations in solution. Such complexes could be useful in biology and medicine sensing, and phosphine-terpyridyl gold(I) complexes are good candidates because of them photophysical properties and structure architecture. Herein we report synthesis of three novel phosphine-terpyridyl gold(I) **(1-3)** complexes (Scheme 1). All novel compounds obtained were characterized by $^1$H and $^{31}$P NMR spectroscopy, single crystal X-ray diffraction analysis, ESI mass spectrometry and elemental analysis. Optical and photophysical properties of **1-3**, namely UV-vi, emission and excitation spectra, and excites state lifetimes have been carefully investigated.



*Scheme 1. Synthesis of the novel gold(I) complexes.*

The authors greatly appreciate financial support from the Russian Science Foundation, grant 16-13-10064. The work was carried out using equipment of Centres for Magnetic Resonance, for Optical and Laser Materials Research, for Chemical Analysis and Materials Research, and X-ray Diffraction Centres (Research Park of St. Petersburg State University).

# Catalytic cycloadition of *N*-vinylpyrroles to nitrones and azomethine imines containing the isoquinoline fragment

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The isoquinoline fragment is an important structural part of a number of alkaloids and biologically active substances [1]. Previously, catalytic reactions of *N*-vinylpyrroles with acyclic nitrones and azomethine imines have been studied by our research group. It was shown that the reaction between pyrroles and both types of dipoles can proceed as formal (3+3)-cycloaddition in the presence of Lewis acids [2].

The aim of this work is to investigate an ability of proceeding the interaction of dipoles containing the isoquinoline fragment with *N*-vinylpyrroles by path of (3+3)-cycloaddition in the presence of $Ni(ClO_4)_2*6H_2O$ (Fig. 1).

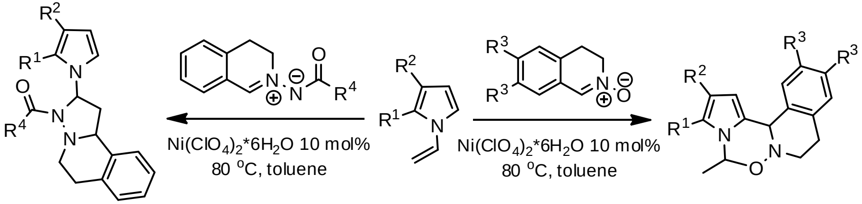

*Fig. 1. The paths of the reactions of catalytic cycloaddition.*

It was found that mixture of diastereomeric products of formal (3+3)-cycloaddition of pyrroles to nitrones is formed. In contrast, (3+2)-cycloaddition is carried out in the case of the interaction of pyrroles with azomethinimines. All products were obtained with good yields.

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# Physico-chemical properties of $C_{70}$-Thr derivative aqueous solutions

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Fullerene derivatives and in particular the light fullerene derivatives with amino acids are very perspective compounds due to possibilities of practical application in biochemistry and medicine [1–3]. For example, they can be used as a lead compounds of anticancer, neuroprotective, antiviral drugs and possess antimicrobial and antioxidant activities. At the same time for realization of biomedical potential of these compounds it is important to carry out investigation of physico-chemical properties and to find correlation between the structure of fullerene derivatives and there properties in solid state and in solutions.

This study is devoted to physico-chemical investigation of the $C_{70}$-Thr aqueous solutions. In the framework of our research, we measured densities ($\rho$), viscosities ($\eta$), refraction indexes ($n_D$), and surface tention ($\gamma$) in a wide range of temperatures and concentrations. Experimental data on size distribution and $\zeta$–potentials of the $C_{70}$-Thr associates in aqueous solutions were obtained in the concentration range 0.001 – 5 $g \cdot dm^{-3}$ at 298.15 K. Using experimental data on the decreasing of the ice crystallization temperature in the $C_{70}$-Thr – water binary system, the excess thermodynamic functions were calculated. Additionally, the structural and dynamic characteristics of the $C_{70}$-Thr – water binary system were obtained on the basis of molecular dynamics method.

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# A novel strategy for selenium determination in dietary supplements samples

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As an important microelement, selenium has a biological influence on the different human bodies' systems, therefore selenium is widely used as a part of dietary supplements. However, at high concentrations this element is toxic, and also able to accumulate in the human body, which can lead to allergic reactions, poisoning, and even cancer. Therefore, there is a need to control the quality of dietary supplements in order to detect the excess content of selenium, which threatens the health and life of the consumer [1].

A novel strategy for selenium determination in dietary supplements samples based on analyte hydride generation with following sorption on magnetic nanoparticles has been developed. The scheme includes three steps. In the first step selenium generation and sorption on magnetic nanoparticles was performed in specially developed vessel. In the second stage, the oxidized form of selenium was eluted from the magnetic nanoparticles, and finally, the analyte was determined by electro thermal atomization-atomic absorption spectroscopy. New technique can be offered as an effective method for the quality control of food samples due to large adsorbing surface of $Fe_3O_4$-based composite nanoparticles providing high selenium concentration from the gas phase.

Scientific research was performed at the equipment by the Research Park of St. Petersburg State University.

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# Stereocontrolled synthesis of pyrrolofullerenes – promising materials for photovoltaics

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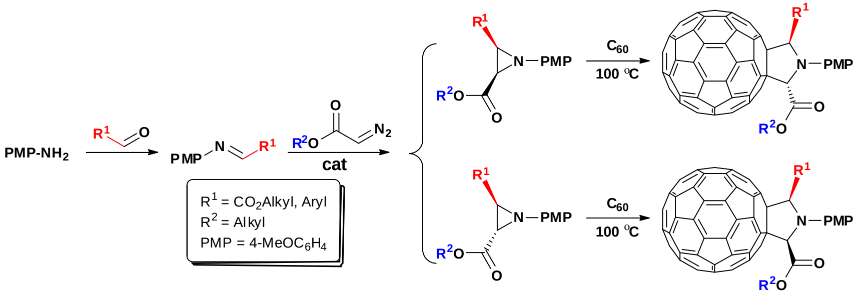
Fullerene derivatives are often used as an acceptor phase in the production of solar cells based on organic compounds. However, the effective use of fullerene derivatives requires proper functionalization by introduction of suitable number of functional fragments having appropriate relative spatial orientation to endorse the desired physical properties to the new molecule. Unfortunately, at the moment there is no theory which could predict the effectiveness of using any $C_{60}$ derivative in photovoltaic devices. Taking this into account, the work aims to expand the empirical base for determining the correlation of "structure-properties" relationship to enable the implementation of rational design of fullerene-based photoactive materials in the future.

This work is devoted to the synthesis of 1'-, 2'-, 5'-substituted *cis*- and *trans*-pyrrolo[3',4':1,9]fullerenes and testing new compounds as photoactive components of converters of light energy into electric power. According to the scheme below, from the appropriately substituted aziridines and fullerene $C_{60}$, adducts containing various alkoxycarbonyl and aryl fragments were obtained.



It was shown that the obtained pyrrolofullerenes can compete with the most common derivative of $C_{60}$ - $PC_{61}BM$ as acceptor component of the active layer in porphyrin-fullerene based photovoltaic cells.

Scientific research was performed using the equipment of the Research Park of St. Petersburg State University «Center for Magnetic Resonance» and «Center for Chemical Analysis and Materials Research».

# Hydroxylamine as an ammonia equivalent: novel entry into trans-*NH*-tetrahydroisoquinolonic acid esters via $TiCl_3$-promoted deoxygenation of *N*-hydroxylactams

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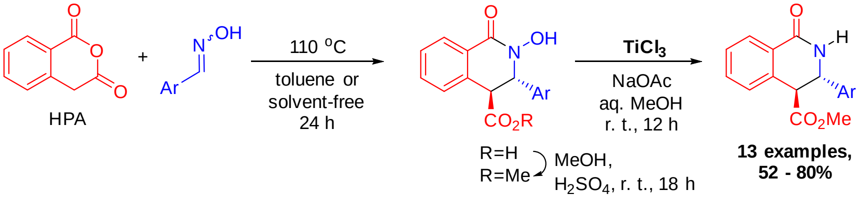
The formal [4+2] cycloaddition of cyclic anhydrides and imines - Castagnoli-Cushman reaction (CCR), offers a facile access to structurally diverse, polysubstituted lactams [1]. Employing homophthalic anhydride (HPA) in this reaction gives rise to tetrahydroisoquinolonic (THIQ) acids (often as a single *trans*-diastereomer) which are facile scaffolds for the design of biologically active compounds most prominently exemplified by anticancer clinical candidates *indotecan* and *imidotecan* [2]. Systematic exploration of the structure-activity relationships around this (as any other) scaffold mandates that either of the periphery substituents can be independently replaced with hydrogen. Previously in our group, it was shown that an introduction of formaldehyde imines in the CCR with HPA results in formation of 3-unsubstituted THIQ acid [3]. In continuation of these efforts, we were also interested in exploring 2-unsubstituted THIQ acid scaffold. However, the existing literary examples turned out to be not universal and not atom-economic [4]. Based on our recently published of new approach to *N*-hydroxy THIQ acids via the CCR of unprotected oximes [5], we are proposing a new atom-economic method for obtaining 2-unsubstituted THIQ acid via deoxygenation by aqueous $TiCl_3$. We successfully applied a three-stage protocol and obtained 13 *NH*-lactams with good yields.



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# Design of a series of isostructural crystals and co-crystals with palladium(II) isocyanides complexes assembled by halogen bonding: isostructurality through chloro/bromo/iodo exchange

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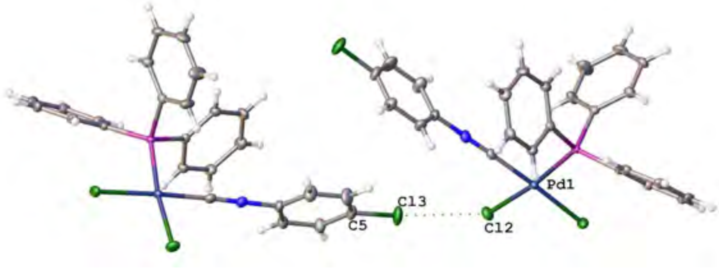
The ability to predict and control the structure of crystals is one of the most important problem in crystal engineering [1]. Reliable way to solve the problem is synthesis of isostructural compounds, in particular those with isostructural halogen exchange stabilized by halogen bonding (XB). Owing our group interest in the non-covalent interactions in platinum group metal complexes [2], we report herein the first example of triple isostructural halogen exchange in organometallic compounds stabilized by XBs.

The complexes *cis*-$[PdCl_2(CNR)(PPh_3)]$ (**5**–**7**) were synthesized by the interaction of $[Pd_2Cl_4(PPh_3)_2]$ with isocyanide in $CH_2Cl_2$ at RT [3] with 92–95% yields and characterized by ESI$^+$ HR-MS, IR and NMR $^1H$, $^{13}C\{^1H,^{31}P\}$, $^{31}P\{^1H\}$ spectroscopy. Complexes **5**–**7** were crystallized from $CH_2Cl_2$ solutions in unsolvated isostructural crystalline form. All the obtained structures contain the same crystal systems and space groups and also almost equal parameters of the unit cells.



**Acknowledgements**. The work was supported by the Russian Foundation for Basic Research (grant 16-33-60123, 18-33-20073) and Grant Program of the President of Russian Federation (Grant MK-4457.2018.3). Physicochemical measurements were performed at the Center for Magnetic Resonance, Center for X-ray Diffraction Studies, Center for Chemical Analysis and Materials Research and Chemistry Educational Centre (all belong to St. Petersburg State University).

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# Obtaining and properties of cobalt containing polymer catalyst

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The purpose of this work is to obtain a fibrous cobalt-containing catalytic material and the study of its surface topography and catalytic activity.

Film samples based on the modified PAN, treated with an aqueous solution of the metal salt [Co (NH3) 6] Cl3 were used as samples of the studies. The following ratios of process parameters were taken into account during sample preparation and subsequent research: the processing time of the modified material with a solution of trivalent cobalt salt (1, 3, 6, 10, 15, 20, 25, 30, 60, 90,120, 240, 480, 960 and 1920 min) , the salt concentration of trivalent cobalt (50 g / l), the concentration of the dye acid blue (45 - 10 g / l), the mass of the sample of catalyst (0.6 - 1.7 g), temperature 20 ° C, pH = 2.

To study film samples, we used the methods of IR spectroscopy on a Fourier spectrometer FSM 1201 and electron microscopy on a JEOL JSM-6390 scanning electron microscope to obtain data on the mechanisms of coordination and the distribution of metal on a polymer carrier. To study the catalytic activity of metal-containing polymer catalysts, the acid blue dye 45 oxidation method was used according to the method described in the source [1]. The experiments were carried out at air flow rates, which: firstly, provided the excess of stoichiometric oxygen required for complete oxidation of all components of the reaction; secondly, they formed a complete mixing mode in the reactor. Determination of the dye destruction was performed using UV spectroscopy on a Specord M-40 spectrophotometer.

The results of the study showed that the best properties are shown by samples subjected to processing for 10 minutes. Data on the determination of cobalt in modified films increase its quantity with an increase in processing time from one to ten minutes. The obtained kinetic parameters indicate the occurrence of catalytic oxidation processes in the diffusion region.

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# Synthesis, Characterization and Photophysics of Luminescent Ir(III) Phosphine Complexes

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Nowadays organometallic iridium(III) complexes attract a significant interest due to their efficient luminescence and rich photophysical properties. This type of compounds is applicable in OLED technology, bioimaging and luminescent microscopy [1]. Herein we report on a series of cyclometalated iridium(III) complexes bearing phosphine and chloride ligands **1-3** (shown in Fig. 1). The compounds were obtained and characterized by $^{1}$H-, $^{31}$P- NMR spectroscopy and single-crystal X-ray diffraction analysis.

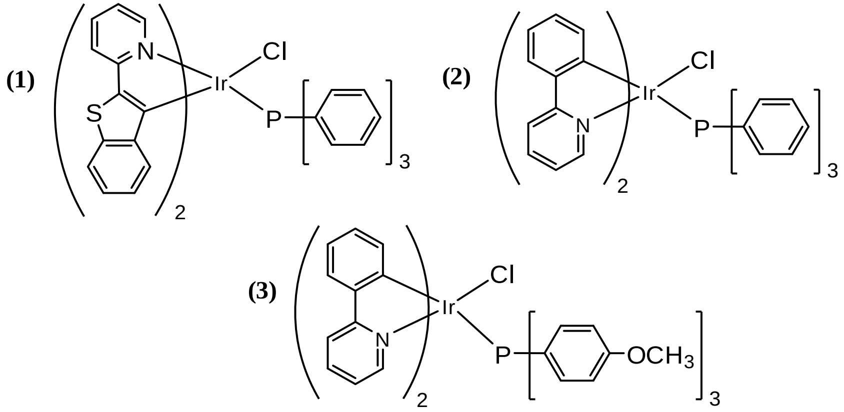

*Fig. 1. Structures of the investigated iridium complexes.*

For all complexes absorption, excitation, emission spectra and quantum yields were measured to study the impact of ligand environment properties onto photophysical characteristics of the compounds obtained.

**Acknowledgements.** Financial support from Russian Foundation for Basic Research (18-33-00954) is gratefully acknowledge. The work was carried out using scientific equipment of St. Petersburg State University Research Park: Centers of Magnetic Resonance, Chemical Analysis and Materials Research; and the X-ray Diffraction Centre.

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# Equilibrium between ItBu·AlH3 isomers: structural and NMR spectroscopic investigation

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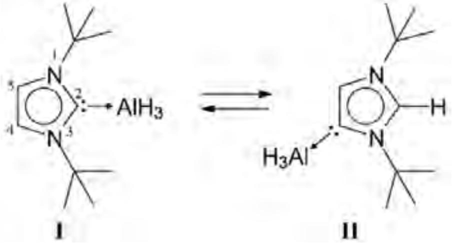
Stable N-heterocyclic carbenes (NHCs) represent very efficient tools in the stabilization of various metal centers due to their strong donor properties [1]. Crabtree and co-workers in 2001 reported the first transition-metal complex with an imidazol-2-ylidene-type NHC binding to a metal center through the C4 carbon, forming so called "abnormal" NHC species [2]. Known examples of such "abnormal" complexes have been discussed in a recent review [3].



*(1)*

Here we report the unprecedented complex I$^t$Bu·AlH$_3$ (**II**), in which sterically unhindered Lewis acid AlH$_3$ coordinates to the C4 carbon of the imidazole ring. **II** was obtained along with "normal" isomer **I** by the reaction between LiAlH$_4$ and I$^t$Bu (I$^t$Bu − 1,3-di-tert-butylimidazol-2-ylidene). The molecular structure of **II** was determined by single crystal X-ray diffraction. The equilibrium constants of process 1 in the gas phase, benzene, THF and CH$_2$Cl$_2$ were computed using DFT (B3LYP/def2-TZVP level of theory). The obtained results indicate that with the increase of the polarity of the solvent the equilibrium shifts toward the formation of "abnormal" isomer **II**. Experimental NMR data in these solvents are in agreement with computational results.

Financial support from SPSU-DFG grant 12.65.44.2017, SPSU grant 28213092 and equipment of the "Centre for Magnetic Resonance" and "Computer Resource Centre" of SPSU are gratefully acknowledged. We are grateful to Michael Weinhart (University of Regensburg) for help with X-ray structure determination of **II**.

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# Dilational surface properties of DNA/surfactant and DNA/polyelectrolyte aqueous solutions

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The formation of complexes between DNA and oppositely charged surfactants and polyelectrolytes has attracted significant attention because of their use in the course of DNA extraction, purification, the preparation of highly organized hybrid bioinorganic nanostructures, and the construction of DNA chips [1]. The application of the complexes for nonviral gene transfer is probably of special importance. The corresponding technological and biomedical interest resulted in extensive investigations of DNA−surfactant and DNA-polyelectrolyte interactions in the bulk phase of aqueous solutions.

In this work the dynamic surface properties of DNA/cetyltrimethylammonium bromide (CTAB) and DNA/poly(methylalkyldiallylammonium chloride) (PMADAAC) aqueous solutions at the solution/air interface were studied by the surface tensiometry, dilational surface rheology, atomic force microscopy, infrared absorption−reflection spectroscopy and ellipsometry. Measurements of the kinetic dependencies of the surface properties gave a possibility to discover the time intervals corresponding to the coexistence of two-dimensional phases. These observations indicate a phase transition of the first order in DNA/CTAB adsorption layers. The application of a few experimental techniques allowed elucidation of the structure of coexisting surface phases and determination of four main steps of the adsorption layer formation in DNA/CTAB solutions. The same approach was also applied to the adsorption layers of the complexes between DNA and cationic polyelectrolytes. The results indicate strong interactions between the components in the surface layer.

**Acknowledgements**. This work was financially supported by the Russian Foundation of Basic Research and the Ministry of Science and Technology of Taiwan (joint project RFFI-MSTT no. 16-53-52034 MHT_a).

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# The new method to afford 3,5-diarylfuran-2(3H)-ones using acidic zeolites CBV-720

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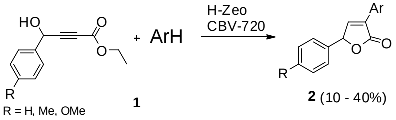
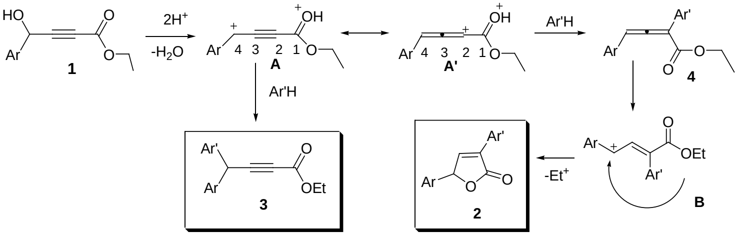
3,5-Diarylfuran-2(3H)-ones are bioactive compounds. By this moment, it is known that they have moderate activity against filamentous fungi. Also they are metabolites from Streptomyces griseus and angelicalactone **[1]**.

These 3,5-diarylfuran-2(3H)-ones were afforded by some approaches: tellurium/lithium exchange mediated synthesis, cyclohydrocarbonylation of substituted alkynes catalyzed by immobilized Co-Rh heterometallicnanoparticales and a facile solid-phase synthesis from polymer-supported selenocarboxylic acids **[1-3]**. Herein, we report a new method for preparation of these substances starting from alkyl esters of 4-aryl-4-hydroxybut-2-inic acids. Zeolites are promising substances for synthesis, because they are an environmentally friendly and renewable resource.



Zeolites CBV-720 are used in this reaction as Brønsted/Lewis acid. In the first stage of this reaction, the hydroxyl group is protonated in compound **1**, followed by dehydration, the cation **A** is formed. The latter has two electrophilic centers, it can be represented as two resonant forms **A** and **A`**. Further, as a result of interaction with arene Ar`H at the propargy position of **C4**, compound **3** is formed. In the case of reaction with the arene at the electrophilic center **C2**, cation **A** gives allene **4**. The latter is protonated, forming cation **B**, which cyclizes to furanone **2**.



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# Automated screening of chemical space for screening and optimization of catalytic reactions in the liquid phase

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Modern quantum chemical methods have become practical tools for studying complex chemical processes at the molecular level. One can readily compute standard state thermodynamic and kinetic parameters for reasonably large systems with good accuracy and reasonable computational resources using DFT methods. The combination of DFT methods, statistical thermodynamics (ST) formalism, and advanced continuum solvation models (CSMs) as Cosmo-RS allows translating the intrinsic energetics (electron energies) into the condition-dependent free energy functions for the description of the behavior of complex systems under the experimental (operando) conditions.

Computing free energy functions (or surfaces, FES') may become a tedious task if one needs to vary all model parameters as reactant and product concentrations, temperature, pressure, solvent, etc. relevant to experimental conditions. Thus, our goal is to create a universal automated platform for systematic analysis and prediction of the behavior of complex chemical systems via the automated combination of DFT and ST calculations with CSMs.

We created scripts combining ORCA computations [1] with COSMOtherm program [2] (COSMO-RS CSM). Obtained data from the ORCA output could also be recalculated for new temperature and pressure values applying the ST formalism. The program allows calculating the Gibbs energies of reactions in the complex multicomponent solutions as well as complex solvent systems. The computed FES' can readily be visualized with the embedded code. One can plot FES' as heatmaps with the embedded code as well. The program code was written in Python 3 and tested on Linux_x86-64 workstations.

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# Changes in structure and color centers formation in alkaline niobo-phosphate glasses under the femtosecond laser irradiation

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Multicomponent phosphate glasses are a promising optical material due to its structure and physical and chemical characteristics. Laser becomes a powerful tool for local changes in the properties of a glassy material. Such modified glass is used to create calibration elements, photonics elements of active media of high-power lasers and diffraction gratings. Depending on the wavelength and mode of exposure, various thermomechanical effects, structural processes, and photochemical reactions can be observed. However some patterns of interaction of laser radiation with matter have not yet been fully studied. E.g. the dependence of laser-induced changes on the type of alkali metal added has not been studied previously. Such study can opens up prospects for the creation of materials with desired properties.

Glasses of the $Li_2O$-$Na_2O$-$K_2O$-$P_2O_5$-$Nb_2O_3$ system were synthesized and modified with laser radiation. The laser modification was performed in a volume by a femtosecond pulsed titanium-sapphire laser in two modes: with a pulse repetition rate of 180 kHz and with a pulse repetition rate of 76 MHz. The structural features of glasses were studied using Raman spectroscopy. Color centers (CCs) were investigated by light absorption spectroscopy.

Studies revealed that in the case of low-frequency laser modification the number of CCs increases with an increase in the added alkali metal radius to lithium phosphate glasses. Structural changes are not significant. But in the case of high-frequency laser modification, the opposite is true. The number of CCs increases with decreasing of added alkali metal radius. Structural changes according to Raman spectroscopy can be associated with an increase in the length of polyphosphate chains.

The fact that the dependence of the optical density of CCs on the type of alkali metal added has the opposite character in the case of high-frequency and low-frequency modification means that the interaction of laser radiation with matter occurs through different mechanisms. In this work the authors offer models that can explain the reason for such results.

**Acknowledgements.** The authors highly appreciate the contribution by Kalinichev A.A. and Prof. Sokolov I.A.

## Gaseous oxyacid salts of germanium, tin and lead

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Studying of processes taking place in materials exposed to high temperatures is a challenging issue which is important both practically and theoretically. High-temperature mass-spectrometry is a unique technique which allows one to determine qualitative and quantitative vapor composition in a wide temperature range making it possible to obtain thermodynamic characteristics of gaseous species.

Gaseous oxyacid salts can be observed in vapor over two oxides vaporizing in the same temperature range and having different acid-base properties. The larger is this difference, the more thermodynamically stable is the salt.

The present work is a continuation of the thorough study of vaporizing processes in complex oxide systems. For each system it was necessary to create conditions of coexistence of gaseous oxides in vapor. Our aim was to observe the formation of a gaseous oxyacid salt and to calculate its standard enthalpy of formation, $\Delta_f H^0$. Thermodynamic properties and structures of gaseous salts were studied by several quantum chemical computational methods as well.

We synthesized the following gaseous salts of 14-elements (Ge, Sn and Pb): germanium vanadate $GeV_2O_6$, borate $GeB_2O_4$ and molybdates $GeMoO_4$, $GeMo_2O_7$; tin vanadate $SnV_2O_6$, borates $SnB_2O_4$, $Sn_2B_2O_5$ and molybdates $SnMoO_4$, $Sn_2MoO_5$, $SnMo_2O_7$; lead phosphates $PbPO_2$, $PbPO_3$, $PbP_2O_6$ and tellurates $PbTeO_3$, $Pb_2TeO_4$. $\Delta_f H^0$ values calculated from the experimental data were in agreement with those ones obtained theoretically for all these salts. Thermodynamic data obtained for gaseous lead salts allowed us to estimate $\Delta_f H^0$ and $\Delta_{at} H^0$ for lead polonates $PbPoO_3$ and $Pb_2PoO_4$ with high accuracy.

Thermal stability of gaseous salts increases from germanium to lead in according with the Periodic law.

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# Development of magnetic chitosan microcarriers for oral protein delivery

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Chitosan is widely studied in biotechnology as efficient vaccine adjuvant, bactericide medicine and biocompatible material for various mucosal delivery systems. Modification of chitosan by magnetic material in nanosized form opens new opportunity in MRI diagnostic of drug therapy and tumor hyperthermia.

The magnetite chitosan microspheres (CMS) were prepared by cross-linking with tripolyphosphate (TPP) and following administration of iron oxide nanoparticles (NPs). In brief, chitosan was dissolved in 1% acetic acid [1]. Microspheres were fabricated by adding cross-linker TPP solution at constant stirring. Magnetite NPs were prepared by co-precipitation from iron salt solutions by increasing pH 10 at $80^0$C in inert $N_2$ atmosphere.

A bovine albumin (BSA), somatropin (SOM) were supplemented to CMS dispersions in process of substantial sorption by CMS during 24 h [2]. The loading protein efficiency was estimated from difference between the total protein amount and non-included protein in supernatant after dialysis. The protein release from loaded CMS was studied in vitro by exposure CMS into aqueous buffer solutions.

The observed protein encapsulation was satisfactory for further oral delivery to animal model. The primary trials show the ability to avoid the enzyme protein destruction in acid environment of stomach.

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# Characterization and separation performance of novel pervaporation membranes for biobutanol purification

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Pervaporation is one of the best methods of separation, concentration, and purification of liquid mixtures, including azeotropic and thermally unstable liquids. This way of separation is characterized by low energy consumption, compact equipment, and ecological friendliness. In view of the limited range of industrial membranes, it is important to search membrane materials with high exploitative characteristics. In the present work, there were obtained novel polymer membranes based on polybenzoxazinone and its prepolymer polyamic acid, which demonstrate high thermal and chemical stability.

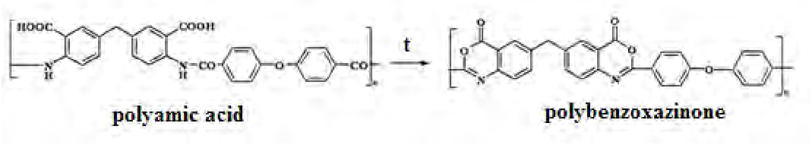

*Fig.1. Transformation of polyamic acid to polybenzoxazinone.*

The aim of the research was an investigation of physicochemical properties and transport characteristics of the membranes in the processes of n-butanol and n-propanol dehydration by pervaporation. The problem of separation of n-butanol – water mixture is of current importance due to the wide use of n-butanol as biofuel base and industrial solvent.

Mass transfer of alcohols and water through the membranes was studied by sorption and pervaporation tests at 20 °C. Thermogravimetric analysis, differential scanning calorimetry and scanning electron microscopy were used to investigate heat resistance and structure of the membranes.

In the course of pervaporation experiments, it was found that the polybenzoxazinone membrane produces permeate enriched with water while the polyamic acid membrane shows poor selectivity but higher permeability. Thus, the obtained membrane based on polybenzoxazinone showed high efficiency in the separation of both water – alcohol mixtures in a wide range of concentrations.

**Acknowledgements.** This work was carried out with the financial support of the Russian Science Foundation (RSF) (grant 18-79-10116).

# Glass formation of $Ag_2Se – GeSe_2 – As_2Se_3 – Sb_2Se_3$ system

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In modern chemical physics the processes that proceed on interphase boundaries are particularly interesting. However, the research can be challenging due to a great number of parameters that affect this process (interdiffusion, the difficulty of defining of effective surface, the degradation of lattice etc.).

As an object of study in our work we used samples of glass, consisting of silver, germanium, arsenic, and antimony selenides. In amorphous samples the difficulties, connected with realignment of lattice, are absent. Moreover, the presence of germanium within the $Ag_2Se – GeSe_2 – As_2Se_3 – Sb_2Se_3$ system leads to wide glass transition range, while the presence of arsenic and antimony leads to amplification of the structure and decrease of the softening point. With the help of silver selenide it is possible to control interdiffusion of the samples on interphase boundaries.

The relation between the temperature change of glass softening point and the change of its chemical composition was set. Obtained glass samples have resistance to crystallization enough to prevent the crystallization of contacting nanolayers of silver selenide.

This research was carried out with financial support of Russian Foundation of Fundamental Research [grant № 17-03-00121].

# New approach to the formation of physically adsorbed capillary coatings consisting different polymers (nanosponges, highly fluorinated polymers)

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Different modifiers (such as surfactants or water-soluble polymers) are used in capillary electrophoresis in order to reduce the analysis time, increase separation selectivity or prevent analytes sorption. Capillary coatings are divided into two main categories depending on the interactions with the capillary wall: the so-called dynamic coatings and permanent coatings. This work describes the application of hydrophilic ionic polymeric nanosponges [1] containing alkylated pyridinium fragments and highly fluorinated polymers with -$NH_2$-groups as physically-adsorbed coatings of fused silica capillary walls.

For the first time it was established that nanosponges provide reversed electroosmotic flow (EOF) after flushing the capillary with their diluted solution for more than 5 minutes (concentration of nanosponges 0,26 mg/ml for functional groups). Nevertheless, approach included filling of the fused silica capillary with nanosponges solution with higher concentration for 2 hours and more provided more stable EOF value. For carboxylic acids separation (formic, acetic, succinic, malic, tartaric, oxalic) were used capillaries modified by nanosponges with molecular masses 100 and 40 kDa. It was established that strong interaction of modifiers with carboxylic groups complicates determination of tribasic acid (citric acid). Obtained results were compared with separation of carboxylic acids on capillaries modified by nano-sized anion exchanger, which was discussed in our previous research [2]. It was established that adsorption of highly fluorinated polymers containing $NH_2$-groups on the capillary walls previously covalently modified by fluorinated chlorosilanes increases separation selectivity of catecholamines. Selectivity increasing is achieved due to prevention of catecholamines sorption as a result of silanol groups blocking.

**Acknowledgments.** The work was supported by RFBR (grant no. 17-03-01282_a and 18-33-01091 mol_a). The authors are grateful to the Chemistry Educational Centre, Research park (SPSU).

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# Densities, dynamic viscosities and refractive indices of Amino Acid Ionic Liquids based on L-Lysine $[C_n mim][Lys]$ (n = 2, 4, 6, 8) in aqueous solutions at several temperatures

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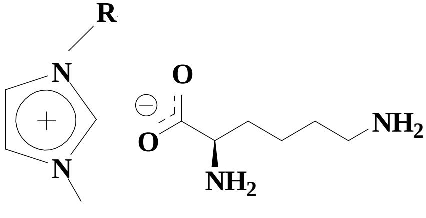
Amino acid ionic liquids (AAILs) have become one of the most rapidly growing new research areas of ionic liquid (IL) and have attracted considerable attention from industry and in the world of science because they are derived from natural ions and are heralded as new natural ILs or bio-ILs. To design any process, involving ionic liquids, it is necessary to know a range of physical properties including viscosity, density, etc.

In this work, a number of AAILs $[C_n mim][Lys]$ (n = 2, 4, 6, 8) based on 1-alkyl-3-methylimidasolium as the cation and L-Lysine as the anion were synthesized and characterized (Figure 1). Experimental dynamic viscosity and density of water + $[C_n mim][Lys]$ have been measured in the temperature range 298.15-328.15 ± 0.05. The results were used to calculate the molar volumes $V_m$, standard entropy $S^0$, and crystal energy $U_{POT}$. The refractive index data were obtained at temperature 298.15 K. The density and the refractive indices decrease in the following sequence: $[C_2mim][Lys] > [C_4mim][Lys] > [C_6mim][Lys] > [C_8mim][Lys]$. It has been found that the change density values with increasing the length of the alkyl chain is less linear in the field of high AAILs concentrations in the water + $[C_n mim][Lys]$ (n = 4, 6, 8) systems.



**$R = C_2H_5, C_4H_9, C_6H_{13}, C_8H_{17}$**

*Fig. 1. Structure of AAILs studied in this work. These are $[C_n mim][Lys]$ molecules where n = 2, 4, 6, 8.*

**Acknowledgements.** The NMR and experimental measurements were carried out on the equipment of the Research Park of St. Petersburg State University (Center for Magnetic Resonance, Center for Diagnostics of Functional Materials for Medicine, Pharmacology and Nanoelectronics). The reported study was funded by RFBR according to the research project № 16-03-00723 a.

# Rh(II)-catalyzed reactions of α-diazoesters with 1,2,4-oxadiazole derivatives

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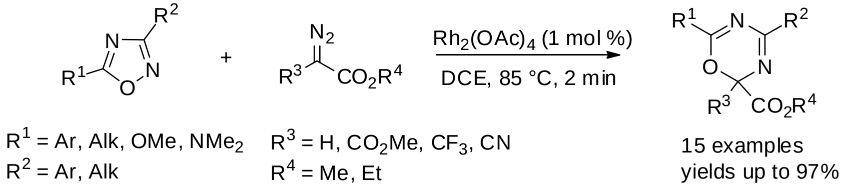
The use of metallocarbenes generated from diazo compounds as convenient building blocks in organic synthesis has intensively developed for many years. Not only these reactive molecules allow to introduce functional groups into a target structure but also serve as a powerful tool for construction of various carbo- and heterocycles.

Quite recently we have shown that 1,2,4-oxadiazole derivatives are capable to undergo cleavage being reacted with rhodium(II) imino carbenes [1]. The aim of present work is to investigate the synthetic potential of 1,2,4-oxadiazoles in Rh(II)-catalyzed reactions with various α-diazoesters.



The reaction of rhodium(II) carbene with aromatic 1,2,4-oxadiazole leads to 2*H*-1,3,5-oxadiazine which is the product of formal carbene insertion into a weak N-O bond of oxadiazole. 2*H*-1,3,5-Oxadiazines are hardly accessible compounds and they are capable to exist in equilibrium with an open-chain form as it was reported earlier [2]. All products obtained during the work were found to exist only in a cyclic form.

In this study, pyridotriazoles were also tested as precursors of metallocarbenes. Furthermore, we have investigated reactions of rhodium(II) carbenes with NH- and N-alkylated 1,2,4-oxadiazole-5(4*H*)-ones.

**Acknowledgements.** We gratefully acknowledge the financial support of the Russian Foundation for Basic Research (Grant Nos. 18-33-00423). This research used resources of "Magnetic Resonance Research Centre", "Chemical Analysis and Materials Research Centre", and "Chemistry Educational Centre" of St. Petersburg State University.

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# Molecular simulation of $CO_2/N_2$ mixture diffusion in LTA-4A zeolite

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According to recent studies, excessive amount of $CO_2$ in the atmosphere may lead to global climate changes. In order to develop robust and scalable methods of reducing the amount of $CO_2$ in the atmosphere, various technologies are being considered. Zeolites have been proposed as potential candidates for adsorption separation of gas mixtures. The efficient use of zeolites for separation and purification requires a detailed understanding of diffusion and adsorption in nanoporous materials under various conditions.

In this work the influence of temperature on diffusion of gases and gas mixtures in LTA-4A zeolite has been investigated by molecular dynamics simulations. Self-diffusion coefficients were determined and diffusion activation energies for gases in zeolite were calculated on the basis of simulation data. Simulations were carried out in the canonical ensemble for temperatures from 500 to 1000 K. The rigid zeolite framework with mobile extraframework $Na^+$ cations contained different amounts of pure nitrogen, pure carbon dioxide or their equimolar mixture (Fig. 1). GROMACS 2016.4 software package was used for simulations and primary processing of the data obtained.

It was found that diffusion of $CO_2$ and $N_2$ in zeolite weakly depends on the amount of adsorbed gas. The activation energy of nitrogen diffusion in the mixture with carbon dioxide is higher than diffusion activation energy of pure nitrogen. Diffusion activation energy of carbon dioxide practically does not depend on the composition of the adsorbed fluid.

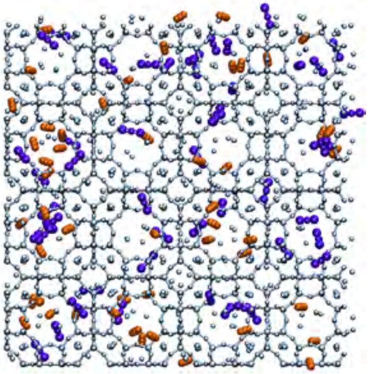

*Fig. 1. Snapshot of the zeolite filled with $CO_2$ and $N_2$.*

# Influence of synthesis route on the layered perovskite-like oxide $K_{2,5}Bi_{2,5}Ti_4O_{13}$ particles size and morphology

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Layered perovskite-like oxides are crystalline compounds consisting of alternating layers of perovskite and layers of another structure (so-called interlayer space). They are widely studied as materials exhibiting such valuable properties as superconductivity, ferromagnetism, ionic conductivity, and photocatalytic activity. [1] Layered perovskite-like oxides are conventionally prepared by high temperature ceramic technique, however it requires long reaction times, high temperatures and does not allow to control the particle size and morphology. Synthesis of perovskite-like oxides by alternative methods allows to obtain particles with controllable size and morphology. For example, sol-gel synthesis allows to obtain porous-materials with large specific surface area. Molten salt synthesis leads to the formation of well crystallized particles with tailorable size and morphology. Hydrothermal method allows to prepare ceramic materials in relatively soft conditions controlling the particle size, morphology and agglomeration degree.

The compound with composition $K_{2,5}Bi_{2,5}Ti_4O_{13}$ has been recently obtained and characterized by Liu et al. [2]. It belongs to n = 4 layered Ruddlesden-Popper phases, where interlayer space is formed by potassium atoms, B-sites of the perovskite slabs are occupied by $Ti^{4+}$ and A-sites are shared by $Bi^{3+}$ and $K^+$. In this work, we investigate the possibility of synthesis of $K_{2,5}Bi_{2,5}Ti_4O_{13}$ by four routes: ceramic, hydrothermal, sol-gel and molten salt methods. Synthesis of the target compound by ceramic method was carried out according to the method described in the previous research [2]. The successful synthesis of $K_{2,5}Bi_{2,5}Ti_4O_{13}$ by sol-gel and molten salt methods is reported for the first time. In case of hydrothermal synthesis, the desired compound could not be obtained under conditions used in the study. The phase composition of the obtained samples was investigated by XRD analysis. The particles morphology and size were compared using Scanning electron microscopy.

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# Electron-deficient 2-azabuta-1,3-dienes as new intermediates in the synthesis of β-lactams

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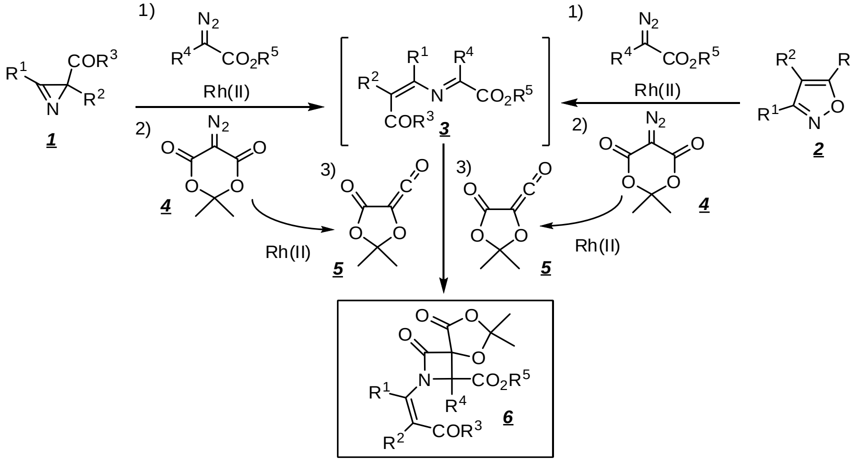
A new method for obtaining highly functionalized β-lactams from azirines or isoxazoles via (2+2) Staudinger cycloaddition electron-deficient 2-azabuta-1,3-diene intermediates has been developed. This reaction, implemented in domino mode or in a sequential mode, involves three stages:

1) a carbenoid-mediated ring-opening of azirine/isoxazole to 2-azabuta-1,3-diene derivative ***3***;

2) generation of ketene ***5*** from diazo compound ***4*** through the Wolf rearrangement;

3) (2+2)-cycloaddition of ketene to 2-azabuta-1,3-diene ***3***.

The possibility of using different diazo compounds in the first two stages of the process significantly expands the range of applicability of the reaction. The most effective catalysts for each of the studied diazo compounds were found and the reaction conditions were optimized. The presented method allows obtaining β-lactams ***6*** with yields of 30-70%.



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# A study of the exhaled breath samples storage in sorbent tubes and Tedlar® gas sampling bags

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The analysis of exhaled breath is technically challenging and has a wide scatter of results depending on the employed methodology. To date there are no standard protocols or recommendations for collection, preparation and storage of exhaled breath (EB) samples for purposes of diagnostics on the basis of EB composition.

The storage of the sample is one of the most significant sample preparation aspects as the application of various offline-methods (such as GC/MS) implies the necessity of samples transportation to the place of analysis conduction.

According to the evaluation of EB samples (from healthy subjects) degradation times in Tedlar® gas sampling bags it appears that within 24 hours the occurring changes in EB sample composition are no higher than instrumental error. However, later on there is a noticeable enrichment with certain components of EB (hexane, heptane, 1-methyl-4-(prop-1-en-2-yl)cyclohex-1-ene, propan-1-ol etc.) as well as a simultaneous loss of others (butanoic and propanoic acid, dodecane). The loss of components seems to be due to the adsorption on the bag inner surface. Basing on the results of microbiology testing it was inferred that enrichment of the sample with particular compounds can be caused by residual vital activities of microorganisms specific for upper air passages.

A better preservation of EB samples can be achieved by storage in sorption tubes hermetically sealed with polytetrafluoroethylene plugs – the composition of the sample remains practically constant within a week.

Thus, the application of sorption tubes for EB samples storage is beneficial for the longtime preservation and transportation of the samples. However, this method increases the time of sample collection. In case the analysis is conducted within 24 hours after the sample collection and (or) includes additional testing with alternative methods the employment of Tedlar® gas sampling bags is preferable.

# Selection and characterization of DNA aptamers to creatinine for DNA-aptasensor design

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Determination of creatinine concentration in biological fluids has a significant importance in means of clinical laboratory diagnostics and sports medicine. Existing methods for creatinine determination have several drawbacks such as low expressivity, expensiveness, interference measurement due to the presence of side compounds in analyzed sample.

To date no application of aptamers for creatinine detection was described in available literature. The emerging test system based on aptamers to creatinine can be seen as a basis of the novel clinico-laboratorial diagnostic methodologies in medicine and sports.

The SELEX (Systematic Evolution of Ligands with EXponential enrichment) method for aptamer selection was used as an approach of oligonucleotide aptamer screening from DNA library. The starting aptamers pool consisted of DNA library 5' TAG GGA AGA GAA GGA CAT ATG AT $N_{30}$ TTG ACT AGT ACA TGA CCA CTT GA 3'.

An analytical PCR was carried out after each round of SELEX in order to control the effectiveness of the selection procedure. Especially the asymmetric PCR was employed for dominant synthesis of single-stranded DNA.

The large scale preparation of aptamers and purification of PCR products by adsorption chromatography were conducted under optimal asymmetric PCR conditions. The enriched pool of ssDNAs obtained after *n* rounds of aptamers selection was amplified with the use of unmodified primers and cloned with BL21 *E. coli.* The target aptamers to creatinine were subcloned into the vector pAL2-T for further sequencing analysis.

This work was supported by St. Petersburg State University Alumni Association grant.

# The contribution of metal center to electrochemical properties of complexes with salen-type ligands

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Organometallic compounds have unique electrical and chemical properties. However, nickel metallic center may not be friendly to the environment, thus the goal of this research was to examine poly[$H_2(CH_3Osalen)$] and poly[$Ni(CH_3Osalen)$] in order to educe the influence of metal on stability and conductivity of a polymer.

Two types of films poly[$H_2(CH_3Osalen)$] and poly[$Ni(CH_3Osalen)$] were synthesized from acetonitrile (AN) solutions containing 0.001 M monomer and 0.1 M $LiClO_4$, in potentiodynamic mode: E = -0.15 – 0.9 V (vs. $Ag/AgNO_3$), potential scan rate $\nu = 50\ mV \cdot s^{-1}$. Films were rinsed with AN and dried. The mass of dried films was determined in order to estimate the specific capacity of films. Cyclic voltammograms of films were registered in 0.1 M $LiClO_4$/AN. Synthesis and electrochemical research were conducted in an argon-filled glove box.

On cyclic voltammograms of poly[$H_2(CH_3Osalen)$] a couple of redox peaks appears at 0.35 V, as well as a shoulder at 0.15 V. For nickel-containing complex poly[$Ni(CH_3Osalen)$], a couple of peaks is seen at 0.535 and 0.435 V and a shoulder at 0.2 V. A sharp peak of reduction within the range of 0.3 – 0.5 V is observed, which is related to $Ni^{3+}/Ni^{2+}$ switching, similarly to the findings of Dahm et al. [1].

Specific capacity was estimated from cyclic voltammograms. It was found that the specific capacity of poly[$H_2(CH_3Osalen)$] is lower compared to the nickel-containing polymer, poly[$Ni(CH_3Osalen)$]: 63 $mA \cdot h \cdot g^{-1}$ and 79 $mA \cdot h \cdot g^{-1}$, respectively.

The conductivity of films was estimated on interdigitated electrodes. It was discovered that the conductivity of poly[$Ni(CH_3Osalen)$] was $4,6 * 10^{-3}\ mOhm^{-1}$ and the conductivity of poly[$H_2(CH_3Osalen)$] film was $0,02 * 10^{-3}\ mOhm^{-1}$.

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# Molecular simulation of $CH_4/N_2$ binary hydrates

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Methane recovered from gas hydrate reservoirs in the permafrost zone can be used as alternative source of energy, thus an efficient technology of its recovery should be developed. One of the most promising technologies is the replacement of methane from the hydrates by injecting the $N_2/CO_2$ gas mixture into the reservoir.

Grand canonical Monte Carlo (GCMC) simulations were used to calculate partial and total occupancies of small and large cages of sI hydrate framework by $CH_4/N_2$ mixtures of various compositions (Fig. 1) and selectivity of the hydrate to $CH_4$. All calculations were carried out at 270 K and pressures up to 90 atm.

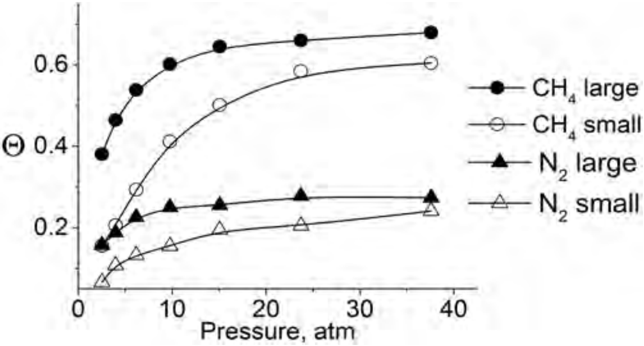

*Fig. 1. Partial occupancies of the small and large cages for the $CH_4/N_2$ (1:1) mixture.*

The main results of the work are:

1. The total cage occupancies of $CH_4/N_2$ mixed hydrate increase with increasing methane content in the gas mixture.
2. The fraction of methane in the hydrate is higher than in the gas phase (for any composition of the mixture).
3. Total cage occupancies of large cages are higher than occupancies of small cages.

This work was supported by the Russian Foundation for Basic Research (grant no. 18-03-00654 A).

# Preparation and characterization of mixed-matrix green membranes based on PVA with surface polyelectrolyte nanolayers

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Nowadays, classical separation methods of liquid mixtures (such as distillation or extraction) are gradually being replaced by the pervaporation method. The pervaporation is one of the dynamically developing methods of the membrane technologies due to its efficiency: low energy consumption, environmental friendliness, compact equipment and high selectivity of the process. However, to separate the required liquids including azeotropic mixtures, mixtures of thermally unstable parts and isomers the right choice of the polymer membrane should be done.

Unfortunately, the majority of polymer membranes have low flux and one of the ways to improve it is the bulk and surface modification of the polymer membranes by inorganic and organic particles. These modified membranes contain the best advantages of combining structures that allows overcoming the trade-off between selectivity and permeability of polymeric membranes.

In the present work the influence of bulk and surface modification on transport properties of membranes made from polyvinyl alcohol was studied. Bulk modification was carried out by incorporation of chitosan and fullerenol into polymer matrix. Surface modification was carried out by layer by layer deposition using four polyelectrolytes: chitosan, polyallylamine hydrochloride, sodium polystyrene sulfonate and polyacrylic acid. The number of PEL bilayers was varied from 2 to 10. As a result it was shown by FTIR, X-ray diffraction, SEM, and the pervaporation separation of 80% isopropanol-20% water mixture that membrane consisting of hybrid layer of PVA-fullerenol (5%)-chitosan (20%) with five polyelectrolyte bilayers (PSS, CS) deposited on it had the best transport properties.

This work was supported by Russian Science Foundation [grant No. 17-73-20060]. The experimental work was facilitated by equipment from Resource Centers: for Nano technology, X-ray Diffraction Methods, Thermal Analysis and Calorimetry, Chemical Analysis and Materials Research Centre and GEOMODEL at St. Petersburg State University.

# Al and Ga metal-organic frameworks with 1,2-bis(4-pyridyl)ethylene: one-, two- and mixed-dimensional networks

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Group 13th metal-organic frameworks (13-MOFs) are prospective materials for sorption, separations, heterogeneous catalysis, sensing etc. [1]. Most of 13-MOFs described are built using poly-carboxylate linkers [2], but there are only a few examples of using N-donors. Thereby synthesis and characterization of new Al- and Ga-MOFs built up with N-donors are important tasks.

All complexes were synthesized by direct interaction of group 13 element trihalides with 1,2-bis(4-pyridyl)ethylene (bpe) under vacuum. Solid state structures of 4 new MOFs were established by single crystal X-ray analysis. In case of initial 1:1 stoichiometric ratio 1D polymer $[Al_3Br_8(bpe)_3]^+[AlBr_4]^-$ ***(1)*** and mixed 1D-2D coordination polymers $[M_2Cl_4(bpe)_5]^{2+}[M_2Cl_4(bpe)_6]^{2+}\ [MCl_4]^-_4$*3bpe (M=Al, Ga) ***(2, 3)*** (Fig. 1) were formed. The presence of large excess of bpe provides isolation of 2D polymer $[Al_2Br_4(bpe)_5]^{2+}[AlBr_4]_2^-$*bpe ***(4)***. Ionic coordination polymers form the porous structures with different pore sizes and shapes.

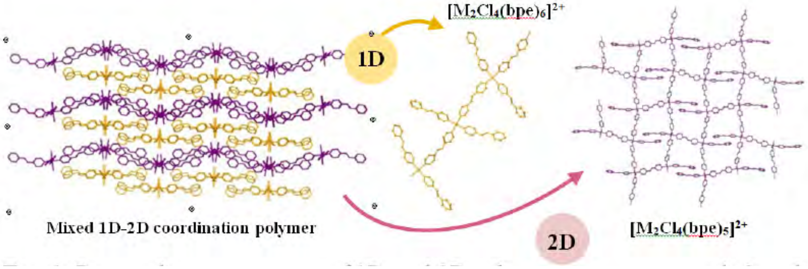

*Fig. 1. Pictorial representation of 1D and 2D subsystems in compounds* ***2*** *and* ***3.***

**Acknowledgements.** We are grateful to M. Bodensteiner, A.V. Virovets and E.V. Peresypkina (University of Regensburg) for the X-ray structure determination.

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# Enhanced oxygen evolution reaction activity of nanoporous $SnO_2/Fe_2O_3/IrO_2$ electrodes with ultralow noble metal loading

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The ability to electrolyze water into its elements in benign conditions at low cost will imply the exclusive use of cheap, abundantly available materials, instead of most advanced catalysts. Iron(III) oxide, the most abundant and least expensive transition metal compound, is one such material [1]. However, $Fe_2O_3$ typically suffers from poor catalytic activity and poor charge-carrier mobility [2-3]. Here, we demonstrate that the combination of nanostructuring with a conductive tin oxide layer and a thin iridium oxide co-catalyst coating can be used to overcome these two limitations and transform $Fe_2O_3$ into a proficient water oxidation catalyst material. Nanoporous composite electrodes are prepared from anodic alumina templates coated with $SnO_2$, $Fe_2O_3$ and $IrO_2$ by atomic layer deposition. Their (photo)electrochemical performance at neutral pH is quantified by steady-state electrolyses and cyclic voltammetry supplemented by the characterization of the electrode nature with X-ray diffraction, X-ray photoelectron spectroscopy and impedance spectroscopy. 20 nm of amorphous $SnO_2$ proves to be ideal as a conductive layer maximizing the efficiency of $Fe_2O_3$. With an additional $IrO_2$ co-catalyst coating of <1 nm light-induced charge-carriers are efficiently separated and consumed in the water oxidation reaction (Fig. 1) yielding stabilized current densities up to $J = 1.9$ mA cm$^{-2}$ (at $\eta = 0.48$ V), which corresponds to a 17-fold increase with respect to pure $Fe_2O_3$.

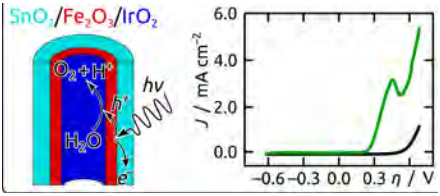

*Fig. 1. Optimized photoelectrochemical oxygen evolution reaction activity of nanoporous $SnO_2/Fe_2O_3/IrO_2$ electrodes relative to pure $Fe_2O_3$.*

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# Organic-inorganic derivatives of protonated layered oxide $HCa_2Nb_3O_{10}$ with glycine and ethanolamine

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Perovskite-like layered oxides are crystalline compounds in which the structure takes place the alternation of two-dimensional blocks (layers) with the perovskite structure, with layers having a different type of structure. Layered perovskite-like oxides are attractive objects research due to the peculiarities of its structure and a number of unique properties, in particular, the ability to intercalate molecules in the interlayer space, ability to ion exchange reactions.

Layered perovskite-like oxides are often subjected to protonation, that is, to the process of substitution of interlayer metal cations for protons. The resulting protonated forms of layered perovskite-like oxides are, in fact, solid acids. When intercalating organic bases and water, the embedded molecules exist in the interlayer space in the form of neutral molecules or ions, forming weak bonds with the layers.

This work is devoted to the synthesis of organo-inorganic derivatives based on protonated and hydrated niobate $HCa_2Nb_3O_{10}$ with monoethanolamine and glycine. The synthesis was carried out in a microwave installation, as well as on a shaker with varying duration, temperature, and concentration. Characterization of the products is performed with an emphasis on their structure and composition.

**Acknowledgments.** This research was supported by RFBR (grants № 16-33-60082 and № 18-03-00915). Authors also are grateful to Saint Petersburg State University Research Park: Center for X-ray Diffraction Studies, Center for Chemical Analysis and Materials Research, Center for Thermal Analysis and Calorimetry, Centre for Innovative Technologies of Composite Nanomaterials.

# Impact of sugar or of ionic liquids as additives on partition behavior of bioorganic compounds in aqueous biphasic systems containing nonionic surfactants

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Nonionic surfactants (NIS) are surface-active compounds that tend to become insoluble in water by being heated above the cloud point temperature (CPT). This particular characteristic of NIS, their biocompatibility and low toxicity gave rise to many applications, specifically to extraction processes (cloud point extraction).

It is well known that various additives (salts, other surfactants [1] etc.) or changes of pH may significantly affect liquid-liquid equilibrium (LLE) in aqueous solutions of NIS. This allows selecting the appropriate conditions for extraction of certain compounds as well as for enzymatic reactions due to their sensitivity to temperature or pH changes. Some ionic liquids (IL) as additives attract researchers' attention due to their low melting points, low toxicity and surface-active properties. Another perspective type of additives are sugars as they demonstrate high biocompatibility that is crucial for bioextraction. Thus, the phase behavior of the solutions containing NIS and sugar or surface-active IL is of special interest.

**In the present work**, the effects of sugar (L-arabinose) and ILs (1-methyl-3-octylimidazolium chloride and bromide) on phase behavior of the aqueous biphasic systems containing NIS (Triton X-114, Tergitol 15-S-7) were under investigation. The choice of NIS could be explained by their wide usage as extracting agents due to low CPTs. Moreover, these systems were considered as reaction media for enzymatic hydrolysis of penicillin G to phenylacetic acid (PAA) and aminopenicillanic acid (APA). The chemical equilibrium of this bioreaction is shifted to the products in case of effective extraction of PAA into surfactant-rich phase, what is of high importance in respect to the synthesis of biologically active penicillin derivatives.

The work was partly performed in Hamburg University of Technology (TUHH). HPLC analysis was carried out on the equipment of the Research Park of St. Petersburg State University, Center for Chemical Analysis and Materials Research and Educational Resourse Center of Chemistry. This study was financially supported by RFBR according to the research project #16-53-12029a.

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# Effect of liposome-microgel complex composition on its stability in water-salt media, aggregation and release kinetics

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Liposome is a spherical particle formed by a lipid bilayer in aqueous media. Due to relative ease of preparation, low toxicity and ability to carry different compounds in both aqueous core and lipid bilayer have made this system most prominent in drug delivery applications. Complexation of liposomes with microgels – networks of cross-linked macromolecules, may allow adding sensitivity to a certain stimulus and ability to codeliver several compounds at once.

Composition of a liposome-microgel complex may be defined as the average number of liposomes adsorbed on one microgel. This parameter may be varied at will since it is simply controlled by the concentrations of liposome and microgel solutions used. However, the liposome-to-microgel ratio controls several key properties of this system.

First of all, when anionic liposomes bind to the surface of positive microgel, the charge is neutralized. If a microgel solution is titrated with a liposome solution then aggregation rate is close to zero at low ratios, because the particles formed are overall positively charged, speeds up at intermediate values since the total charge is not large enough to prevent association, and slows down again when the surface of microgel is fully covered with liposomes.

The constructed system is temperature-sensitive: when microgel is heated to 40-60°C, it significantly shrinks and the adsorbed doxorubicin-encapsulating liposomes release all their contents. Release kinetics are defined by the composition of the complex: doxorubicin is released faster at lower liposome-to-microgel ratios since the number of adsorption sites from which leakage may be accelerated is bigger in this case.

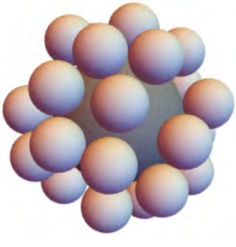

*Fig. 1. Model of a liposome-microgel complex.*

Interestingly, there is no relation between composition and the highest ionic strength at which a complex may be formed. A rather simple explanation may be given: the strength of interaction should be defined by surface charge density. The complex where either a microgel or a liposome carries more charge is expected to sustain its stability at higher ionic strengths when compared to a system where charge density is lower. Thus, the number of adsorbed liposomes has no effect on stability in water-salt media.

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# A novel environmentally-friendly and highly-available extraction approach: HPLC-UV determination of preservatives in food products

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Preservatives play an important role in food industry. However, their excessive use can lead to allergic reactions, anemia and even cancer in humans. Therefore, the determination of these substances in food samples is an important task of food quality control. Taking into account the complexity of sample matrixes sample preparation is strictly required.

The dispersive liquid-liquid microextraction (DLLME) and its different approaches are simple and widely used pretreatment techniques in food analysis.

In this research we developed a new approach, which is called a heating-assisted dispersive liquid-liquid microextraction with organic phase solidification (HA-DLLME-OPS). Menthol has been proposed as a green and cheap solvent for sample pretreatment and applied in this study. The HA-DLLME-OPS assumes the addition of aqueous sample to the extractant solvent (menthol) followed by heating the system what promotes menthol melting and its even distribution in aqueous phase by moving extraction solvent from down to top of the sample and, as a consequence, microextraction of target analytes. After that the obtained mixture was cooled for the solidification of liquid menthol phase, and menthol film formation was observed. The aqueous sample phase remaining under the film was removed via the syringe with needle. Finally, methanol was added to the solidified extractant solvent, thermostated, shaken and the obtained solution containing target analytes was analyzed by HPLC-UV.

The main advantage of this approach in comparison with the classical DLLME is absence of additional disperser organic solvent that usually reduces the partition coefficients of the hydrophobic analytes into the extraction solvent. Also the simplicity of operations, rapidity and low cost can be mentioned as excellences of the developed DLLME-OPS procedure.

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# On the possibility of prostate cancer diagnosis using potentiometric multisensor system

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Prostate cancer (PCa) is the second most common cancer in males and it is one of the leading causes of cancer mortality. According to the statistics of World Health Organization, more than 400 000 cases of prostate cancer are registered in the world every year. Early detection of cancer provides a higher chance of recovery. The common test for prostate specific antigen (PSA) in blood with enzyme-linked immunosorbent assay (ELISA) is known to have quite low sensitivity and specificity. In fact the only reliable way of diagnostics is prostate biopsy. The search for novel non-invasive diagnostics methods is really urgent task.

Potentiometric multisensor systems were already explored in the context of medical studies [1, 2] to distinguish urine samples from patients having various diseases and healthy control groups and these studies yielded quite promising results. The present work deals with exploration of possibility of using potentiometric multisensor systems for the diagnosis of prostate cancer based on measurements in urine samples. If successful, such an approach may provide a faster, a simpler, a cheaper and non-invasive way of prostate cancer diagnostics.

89 urine samples were analyzed with potentiometric sensor array comprising 28 cross-sensitive sensors. 43 samples were from patients with PCa diagnosis, 46 were from healthy male volunteers. The measurement results were processed with various chemometric methods in order to build predictive mathematical models relating sensor response with patient’s status with respect to PCa. The most promising results were obtained with logistic regression providing for classification model with 100% sensitivity and 93% specificity as assessed with independent test set.

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# Light-sensitive glycoseaminoglycan/poly-L-lysine nanogels as vehicles for gene therapy

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Delivery of drugs in the eye and skin is one of the most challenging endeavors faced by the scientist, because both of the targeted organs are well protected by various barriers and defense mechanisms [1].

In our study cationic polymer – poly-L-lysine (PLL), and natural biocompatible glycosaminoglycan – heparin (Hep) have shown some promise in complexing model oligonucleotide (dT(TAMRA)-dA) and *in vivo* delivery. The PLL contains primary aminogroups, which could be used for attachment of the drugs with application of light-sensitive linker (4-(2-chloropropionyl)phenylacetic acid). The sulfate groups of heparin are responsible for strong anionic behavior that causes interpolyelectrolyte complexation with PLL. The size, zeta potential and PDI of nanogels were determined by DLS method to investigate the influence of Hep and PLL concentration ratio and PLL molecular weight (MW) on particle formation and structural characteristics. Morphology of nanoparticles was investigated by transmission electron microscopy. According to results, with an increase in Hep concentration and decrease in PLL MW, the mean size of the Hep/PLL particles gradually decreased from 300 nm to less than 100 nm and tended to balance when the Hep concentration is 5-7 mg/ml and PLL MW is 7850. In general, all of the obtained particles systems were considered moderately stable with the absolute value of the zeta potential was at least 30 mV.

*In vitro* cytotoxicity studies performed with the HEK 293, NIH-3T3, BEAS-2B cell lines showed good cell tolerance for nanogels (up to 0.25 μg/ml for 72 hours). The cellular uptake of the nanogels was investigated by fluorescent microscopy and flow cytometry analysis. These results are in a good agreement, which indicates that the nanogels can be effectively internalized by the cells though the nanogels have fully negatively charged surface, which is generally thought to be adverse to cellular uptake. Thus, a novel approach to gene therapy systems has been introduced in the present work.

The work was supported by G-RISC, funded by the German Federal Foreign Office via the DAAD, and Megagrant of Russian Ministry of Education and Science 14.W03.31.0025.

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# The impact of synthetic parameters on $SnO_2$ nanoparticles sizes in microemulsion method: theoretical and experimental approaches

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Semiconductor materials based on tin dioxide nanoparticles (NPs) may be perspective for gas sensors, supercapacitors, and lithium ion batteries. The functional properties and application fields of $SnO_2$ NPs strongly depend on their sizes and shapes. The most common method to obtain NPs is sol-gel. Its disadvantage is that NPs size regulation is carried out only by calcination process which can lead to a wide size distribution. That is why it is very important to develop another synthetic procedure such as reverse micelle or water-in-oil microemulsion methods. In this case the NPs sizes could be regulated by varying an aqueous droplet diameter.

The work suggests a combination of theoretical and experimental approaches for an investigation of $SnO_2$ synthesis by microemulsion method and a determination of the relation between synthesis conditions and morphological properties of obtained particles.

The impact of polar/nonpolar component volume ratio, surfactant type and concentration, pH values on aqueous droplets and on NPs sizes and reaction yield were studied. The as-prepared samples were characterized by XRD, TEM methods, SSA estimation and Raman spectroscopy.

It was shown that the optimal emulsion stabilization is achieved only in the case of high concentration of ionic surfactants. For the first time the relationship between $SnO_2$ NPs sizes, pH values on aqueous droplets, the charge of surfactant head, and the length of surfactant tail were demonstrated. So we can conclude that electrostatic interactions in the volume of a surfactant stabilized droplet, in which a chemical reaction occurs, have a significant influence on the morphological parameters of the final product. At the moment approaches to experimental and theoretical description of obtained results were developed and optimizing.

**Acknowledgements.** Scientific research was performed at the Research Park of St. Petersburg State University: Centre for X-ray Diffraction Studies, Center for Optical and Laser Materials Research, Centre for Innovative Technologies of Composite Nanomaterials, Chemical Analysis and Materials Research Centre. Authors would like to thank Dr. M.A. Voznesenskiy for numerical evaluation of droplets sizes.

# Synthesis of ketal and acetal linkers for creation of pH-sensitive nanogels

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Today the number of severe diseases could be effectively treated with application of biomacromolecular drugs, as they have high specificity of action and can interact with multiple targets [1]. However, their wide application is limited by their fast rate of inactivation into the organism, as well as by their immunogenicity [2]. These problems could be mounted via creation of special encapsulated dosage form, which allows control over biomacromolecular drug delivery and release at the site of action. In the case of intracellular delivery of siRNAs the sharp release under the influence of certain factors (triggered release) is required. One of the interesting routes to achieve such an "explosive" release is creation of polysaccharide-based nanogels, cross-linked via pH-sensitive links. Such systems could encapsulate biomacromolecules and release them within the intracellular medium, which is known to be acidic. Among different linkers, acetals and ketals deserve special attention, since they give a neutral medium reaction and are potentially non-toxic for the cells after the cleavage [3]. In the current study the synthesis of pH sensitive ketal linker is described.

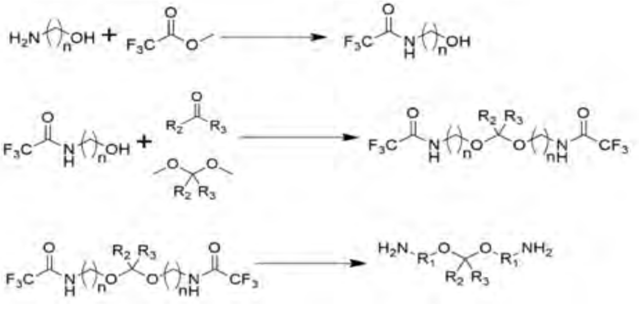

*Fig. 1. General scheme of synthesis of ketal and acetal linkers.*

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# Synthesis of hafnium dioxide nanoparticles for using in oncology

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Radiation therapy is one of the classic methods of treating oncological diseases along with surgery, chemotherapy and immunotherapy. Up to 60% of patients receive radiation therapy at various stages of treatment. Despite its widespread use, this method has limitations, in particular undesirable reactions of perifocal (non-tumoral) tissues [1]. The development of agents that increase the sensitivity of tumor tissues to ionizing radiation is one of the methods for increasing the effectiveness of radiation therapy [2]. This paper proposes the use of nanoparticles of hafnium oxide (HfO2) as radiosensitizers. Such nanoparticles with high electron density, possessing biocompatibility and selective accumulation in cancer cells make it possible to enhance the radiation doze [3] The aqueous dispersions of nanosized $HfO_2$ particles of 50 nm size were obtained and investigated. Phase composition, morphology and distribution of elements in xerosols were studied (Fig. 1). The cytotoxicity of nanoparticles on cell cultures was evaluated. The work was supported by the Grant of Russian Foundation for Basic Research No 18-29-11078.

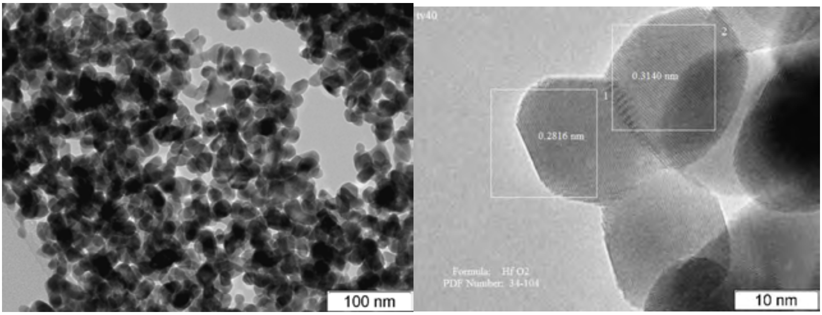

*Fig. 1. HRTEM images of $HfO_2$ nanoparticles.*

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# Mixed $CO_2/N_2$ hydrates occupancy by Monte Carlo simulations

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The combustion of fossil fuels yields enormous amounts of flue gas, which contains mainly nitrogen and carbon dioxide. To avoid the global warming, $CO_2$ should be separated from this mixture and sequestrated in a safe form. To improve existing purification technologies, the fundamental molecular mechanisms of $CO_2/N_2$ mixture separation (particularly, by hydrate formation) should be investigated.

In this work the compositions of binary $CO_2/N_2$ hydrates existing in equilibrium with bulk gas mixtures were obtained by Monte Carlo simulations in the grand canonical (μVT) ensemble at a temperature of 270 K. Five various compositions of $CO_2/N_2$ mixture were considered (10:90, 30:70, 50:50, 70:30, 90:10). The occupancy of both sI and sII hydrate framework structures was studied.

It was found that binary $CO_2/N_2$ hydrates contain more $CO_2$ as compared to bulk gas mixtures for both sI and sII structures. Carbon dioxide predominantly occupies large cages in the hydrate, since the size of its molecule is too big for the small cages. Thus, nitrogen has to fill the small cages of the hydrates. The configuration of sI hydrate framework occupied by equimolar $CO_2/N_2$ mixture is shown in Fig. 1.

This work was supported by the Russian Foundation for Basic Research (grant no. 18-03-00654 A).

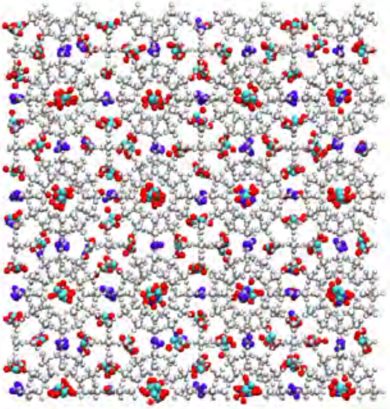

*Fig.1. Snapshot of sI hydrate framework filled with $CO_2/N_2$ mixture (1:1).*

# Synthesis and optical properties of $Eu^{3+}$-doped $SnO_2$ nanoparticles

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Attractive optical properties and high luminescence efficiency of the rare-earth element doped materials open new possibilities for their different practical application e.g. in new light sources, lasers, display and telecommunication devices, energy transformers, sensors, etc. The optical properties of doped materials may come from the energy transitions in the partially filled 4f electronic shell of the rare elements trivalent ions. Among all of them, $Eu^{3+}$ is given particular interest because of the red photoluminescence (PL) at the photon wavelength of approximately 620 nm.

By now as matrices for Eu ions the different spinels (such as $Ca_2P_2O_7$, $SrAl_2Si_2O_8$, $LaTi_2O_7$, $Cu_3Ti_4O_{12}$) are widely used. The problem is that the synthetic procedure is very difficult, and there is an upper limit of dopant concentrations. The main idea of our work is to expand the matrices row by using the material with a rutile structure in which the dopant may be well embedded and distributed.

So, we have chosen tin dioxide, semiconductor with a wide band gap 3.6 eV, as a matrix. Note that partially in all paper about Eu-doped $SnO_2$ the calcination stage, which may lead to the formation the Eu clusters, is conducted.

That is why we have proposed the original synthetic procedure based on (co) precipitation method, and prepared the samples with a Eu concentration from 1 to 50 mol%. The NPs structure and composition were investigated by XRD, TEM methods, SSA estimation, and XPS, FTIR, Raman spectroscopy. The absorbance spectra were also measured, and the band gap values for all the samples were determined. It was shown that the NPs sizes (near 5 nm), shape (sphere) and band gap (3.4 eV) didn’t dramatically change with the increase of the Eu concentration. The study of PL properties indicated that in all Eu concentration range PL quenching was not achieved. The process of organic dyes photodegradation using as-prepared samples is still under study.

**Acknowledgements.** Scientific research was performed at the Research Park of St. Petersburg State University educational resource center of chemistry: Centre for X-ray Diffraction Studies, Center for Optical and Laser Materials Research, Centre for Innovative Technologies of Composite Nanomaterials, Chemical Analysis and Materials Research Centre. The author acknowledge Dr. I.E. Kolesnikov for optical properties measurement and discussion.

# Non-constancy of the bulk resistance of potassium-selective electrodes: a striking puzzle

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Ion-selective electrodes (ISEs) are widely used as potentiometric sensors of ions in various applications from clinical diagnostics to environmental monitoring, to industry and agriculture, and to laboratory practice. According to the existing theory, the ISE response to $I^{z_I}$ ions obeys the Nernst equation:

$$E = E^0 + \frac{RT}{z_I F} \ln \frac{a_I^{solution}}{a_I^{membrane}} \quad (1)$$

Here $E$ is the measured electromotive force (EMF), $E^0$ is its' standard value, R, $T$ and $F$ are, respectively, the gas constant, temperature, and the Faraday constant, $a_I$ stands for the $I^{z_I}$ activity in the sample and in the sensor phase. For practical purposes, only a linear part of the response ($E$ vs. $\log a_I$) is utilized:

$$E = E^{01} + 2.303 \frac{RT}{z_I F} \log a_I^{solution} \quad (2)$$

Obviously, eq. (2) is only valid if $a_I^{membrane} = Const$, otherwise the ISE response is non-linear. In turn, this condition means that ISE membrane composition is constant. Respectively, within the linear Nernstian domain of an ISE response the membrane bulk resistance also must be constant. However, the experimental results obtained with $Ca^{2+}$ and $NO_3^-$–ISEs [1, 2] do not support this theoretical expectation.

We here addressed this striking puzzle using as the model system $K^+$-ISEs with PVC membranes plasticized with di(nonyl)adipate, containing valinomycin as neutral carrier and potassium tetrakis(p-Cl-phenyl)borate as ion-exchanger. Electrochemical properties of the membranes, including the bulk resistance, were measured by means of zero-current potentiometry, chronopotentiometry and electrochemical impedance. Significant dependence of the bulk resistance on the KCl concentration in aqueous solutions was registered, fully analogous to that reported elsewhere [1, 2]. The inconsistency between the existing theory of the ISE response and these experimental observations, tentatively, can be ascribed to the heterogeneity of the membranes due to water uptake from solutions.

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# Diagnostics possibilities of lung cancer using direct breath analysis with electronic nose system based on semiconductor gas sensors

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Treatments outcomes of lung cancer are directly related to the tumour abundance at the beginning of the therapy. Early lung cancer diagnostics is still not solved properly; for more than two thirds of affected people the treatment is initiated already with locally abundant or generalised tumour forms present. Thus, the developing and testing of new relatively inexpensive, simple, and compact screening tools for early non-invasive diagnostic of lung cancer is a highly relevant task for the clinical analytical chemistry. The presence of multiple compounds in the exhaled air provides wide diagnostics possibilities for the breath analysis. VOCs originate from varied biochemical pathways and alterations in these pathways under health disorders leads to the altered VOC profile of the exhaled breath. Along with direct quantification of the VOCs (GS-MS, PTR-MS, etc.) there is another approach to the breath diagnostics, based upon pattern recognition. In this approach the whole multidimensional dataset, obtained by a certain technique, e.g. E-nose, is analyzed as an image, unique for each tested patient. E-nose is multisensory system with a panel of gas-sensitive sensors with a cross sensitivity towards different groups of VOCs. The aim of the current study was to develop an online E-nose based lung cancer diagnostic method using exhaled breath analysis.

This study involved 119 individuals: 65 – lung cancer group, 54 – healthy control group. Exhaled breath samples of the volunteers were analysed using the developed electronic nose system. The dataset obtained, consisting of sensors' responses, was pre-processed and was subjected to a decrease of dimensions by principal component analysis. Training data (75%) was used to fit classification models and test data (25%) was used for estimation of prediction possibility. The performance of the technique developed with e.g. random forest classifier seems to be encouraging for screening purposes (sensitivity – 87.5%, specificity – 100.0%, accuracy – 94.4%).

The results of the current pilot study showed the applicability of the gas-sensitive sensor array for the exhaled breath diagnostics. The discrimination between lung cancer patients and healthy controls was observed with acceptable levels of sensitivity and specificity under online measurement mode. The implementation of E-nose based systems seems very promising for designing the outpatient diagnostic schemes.

# Synthesis and thermal stability of $[Cu_4OCl_6(DMA)_4]$

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Metal organic frameworks (MOFs) are high-molecular compounds formed by transition metal cations and polydentate ligands. The small size of transition metal cations in combination with a large effective charge, as well as the presence in some cases of unfilled d-orbitals provide a strong connection between the metal donor and ligand groups. The most important MOF-based materials characteristics are high porosity, specific surface area, large pore volume and, accordingly, increased adsorption capacity [1].

As inorganic components of frame structures, mainly two-, three- or four-charge cations are chosen, as a rule, transition metals, since the chemistry of complex compounds is well studied for them.

Optimization of the synthesis of such compounds occurs by varying the reagents for the synthesis, their chemical nature, structure, or changing the conditions of the synthesis (for example, temperature and nature of solvents).

In this work we present results of investigation of new inorganic compound that could be applied for preparation of MOFs based on copper-oxygen cluster. We got the cluster $[Cu_4Cl_6O(DMA)_4]$ by crystallization from the ternary system $CuCl_2$-dimethylacetamide-1,4-dioxane. This compound is a cluster in which four copper atoms are interconnected by $\mu^2$-Cl chlorine atoms and by $\mu^4$-O oxygen atom. Thermal destruction of the compound occurs step by step. According to the TGA analysis, there are three main peaks of mass loss: at 180°C (13.92%), 207°C (19.3%) and complete decomposition of the sample occurs at 232°C [2].

**Acknowledgments.** This work was financially supported by the Russian Foundation for Basic Research (project no. 18-33-00636). The equipment of the St. Petersburg State University Research Centers “Centre for Optical and Laser Materials Research”, “Thermogravimetric and Calorimetric Research Centre”, “Centre for X-ray Diffraction Studies”, “Chemical Analysis and Materials Research Centre” and “Chemistry Educational Centre” were used.

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# Partition behavior of L-tryptophan in aqueous biphasic systems of imidazolium-based ionic liquids

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Aqueous biphasic systems (ABSs) containing water-miscible Ionic Liquids (ILs) are considered as a media for liquid-liquid extraction (LLE) of bioactive materials. Such unique properties of ILs as inflammability, low toxicity and possibility for the modification of their chemical structure makes them a good alternative to the most of organic extracting agents.

The main aim of this work is to evaluate the effects of ABS' composition and of IL' structure on the distribution of solute (L-tryptophan) between two liquid phases. ABSs under study contain dialkylimidazolium ILs with halide anions $[C_nmim]Hal$ (where n - number of carbon atoms in the alkyl chain of IL = 4, 6, 8; Hal = $Br^-$ , $Cl^-$) and inorganic salts ($K_3PO_4$, $K_2HPO_4$). As a result, the partition coefficients of L-tryptophan have been investigated (Fig. 1).

These data are helpful to find the ABS with the desired properties, e.g. its extraction capacity, what is one of the major aspects of their application in the field of bioextraction.

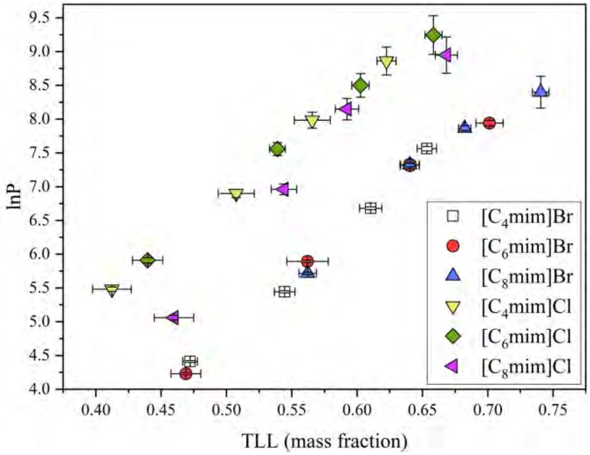

*Fig. 1. Partition coefficients as a function of Tie Line Length (TLL) for the systems* $IL+K_3PO_4+L\text{-}Trp+H_2O$ *at 298 K.*

**Acknowledgements.** The work was financially supported by RFBR (project # 16-03-00723 a). The spectrophotometric measurements were carried out on the equipment of the Research Park of St. Petersburg State University.

# Influence of capping agents on morphology and functional properties of Co and Ni nanoparticles

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It is well known that metal nanoparticles (NPs) have unique magnetic, optical, catalytic and electrical properties, so they have a wide range of applications [1]. Electronic devices, high-density data storage, nanosensors, medicine, catalysis – this is the small part of areas where nanoparticles can be used [2]. It is known that the functional properties of metal NPs are strongly dependent on their sizes, shape and surface composition. Besides, the surface of nanoparticles can be easily oxidized and needs to be protected. Therefore, the synthesis was carried out in organic solvents at atmospheric pressure (polyol method, PM) or under pressure (solvothermal method, SM). To protect the surface and to control the shape and size of NPs capping agents of different nature can be used but their impact on NPs functional properties are not sufficiently studied.

In this work, Ni and Cu nanoparticles were obtained by PM and SM in the presence of different capping agents (phenanthroline (Phen), etidronic (EA), salicylic (SalA), succinic (SucA) acids). The samples were characterized by XRD, SEM, DLS and IR-spectroscopy. ζ-potential values were also determined. The catalytic properties for bare and capped NPs were investigated by high performance liquid chromatography using the reaction of toluene oxidation.

The obtained results showed that capping agents allowed to regulate NPs size and shape in both synthetic procedures. Moreover, the impact becomes more intense in EA, SalA, SucA, Phen row (PM), and SalA, Phen, EA, SucA row (SM). It was determined that oxidation process occurs only for Cu NPs, and leads to different derivates depending on NPs surface composition. In the cases of SalA, SucA (PM) and Phen, EA (PM) capped NPs benzyl alcohol and benzoic acid were obtained correspondently. In the other cases the mixture of derivates was formed.

**Acknowledgements.** Scientific research was performed at the Research Park of St. Petersburg State University: Centre for X-ray Diffraction Studies, Center for Optical and Laser Materials Research, Centre for Innovative Technologies of Composite Nanomaterials, Chemical Analysis and Materials Research Centre.

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# New covalent coatings based on imidazolium ionic liquids for the determination of bioactive compounds by capillary electrophoresis

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Adsorption of analytes onto the inner quartz capillary wall is the effect that lowers separation efficiency. The covalent coating is a good idea solving problem of sorption of positively charge analytes in capillary electrophoresis. Moreover it has advantage such as high reproducibility of results due to creation of stable electroosmotic flow (EOF). Imidazolium ionic liquids can be good functionalizing agent for covalent coatings because it generates anodic EOF and can interact with analytes through π-π interactions, as a result separation selectivity is increased. A method of covalent coatings creation was offered (Fig.1). In the last step butyl bromide, octyl bromide and β-CD were used.

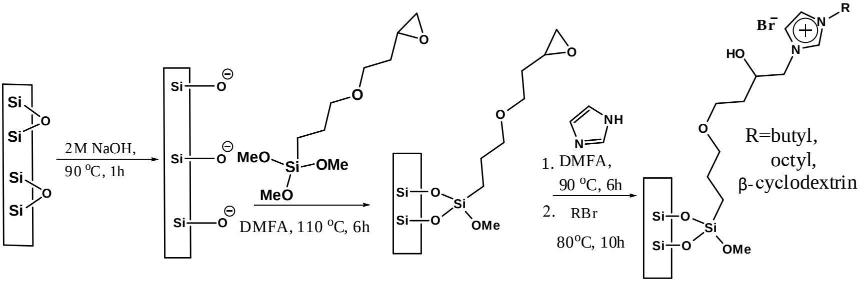

*Fig. 1. Scheme of synthesis covalent coatings based on imidazolium ionic liquids.*

The control of modification degree was performed by measuring of EOF velocity. This coating provided a strong reverse EOF and was stable in pH range 2.0-9.3. The existence of the covalent coating was also confirmed by scanning electron microscopy (SEM). The analytical possibilities of capillary with synthesized coating were studied for separation of model mixtures of biologically active analytes. Various ways of *on-line* preconcentration *(stacking, sweeping, electrostacking)* of target analytes were tested. Stacking efficiency factors over 3000 were achieved. Obtained values of limits of detection in modified capillary allow to determine analytes in sample urine after solid-phase extraction.

The research was performed with financial support of grants RFBR № 16-03-00791-a and 17-03-01282-a with usage of the equipment of Educational Resource Center of SPSU Research Park.

# Kinetics of photoinduced transitions in azobenzenes for pharmacological application

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Photoswitches such as azobenzene derivatives can be optically switched between *trans*- and *cis*- conformations (Fig. 1). These isomers shows different biological activities, what offers an opportunity to control wide range of biological processes by the light. For instance, amphiphilic azobenzenes can target voltage-gate ion channels [1, 2]. It is known that these compounds confer light sensitivity onto retinal ganglion cells in blind mice, which makes them promising candidates as vision-restoring drugs for degenerative blindness treatment [3].

In our research process of photoinduced transition of a series of azobenzenes was studied by the method of time-resolved spectroscopy. The effects of different solvents and acidity on the time of transition between *cis*- and *trans*- conformations were considered. Also, activation energies of processes were obtained.

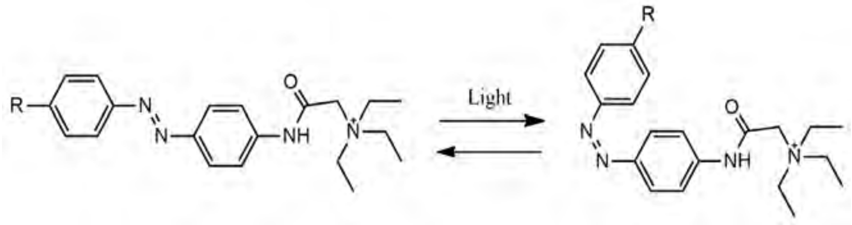

*Fig. 1. Photoswitching of azobenzene between isomers.*

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# Critical phenomena in quaternary reacting system propionic acid – propyl alcohol – propyl propionate – water at 303.15 K

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Researches of phase equilibria in the heterogeneous multicomponent systems with a chemical reaction are in demand in various fields of chemical technology. Studying of such systems is necessary for development of modern, highly-efficient and environmentally friendly methods of synthesis of propyl propionate and for the design of coupled processes, e.g. reactive distillation in industrial scales [1].

This work report data on the solubility and critical phenomena for quaternary reactive systems propionic acid – propanol – propyl propionate – water and two ternary subsystems (propionic acid-propyl propionate-water and propyl alcohol-propyl propionate-water). Previously propionic acid was purified in distillation columns. Data on the solubility and critical area were found by isothermal titration at 303.15 K. In the critical area, blue opalescence was observed. Obtained results for one section quaternary systems are presented on a Gibbs-Rosebom triangle (Fig. 1).

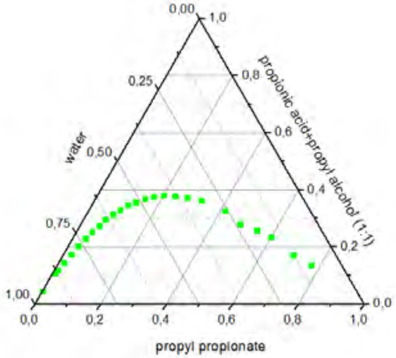

*Fig. 1. Experimental points of solubility in the system propionic acid-propyl alcohol-propyl propionate-water with the ratio of mole fractions of propionic acid and propanol 1:1, at 303.15 K.*

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# New inorganic-organic hybrids based on layered perovskite-like titanates $HLnTiO_4$ and $H_2Ln_2Ti_3O_{10}$ (Ln = La, Nd)

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Ion-exchangeable layered perovskite-like oxides are solid crystalline substances in which two-dimensional nanosized perovskite slabs alternate with interlayer spaces containing alkali cations [1]. Over the last decades, these compounds have been actively studied as materials with practically significant catalytic, photocatalytic, electrophysical and luminescent properties. Protonated forms of layered perovskite-like oxides may be produced by ion exchange in acid solutions. They may react with some organic compounds forming inorganic-organic hybrids – substances consisting of chemically bonded inorganic and organic parts. Thanks to the increased interlayer distance, the hybrids may be exfoliated into monolayers – nanoscale perovskite-structured materials, which are promising catalysts and photocatalysts [2]. However, formation of inorganic-organic hybrids based on layered perovskite-like titanates is not sufficiently investigated.

The present work is devoted to synthesis and investigation of inorganic-organic hybrids of protonated titanates $HLnTiO_4$ and $H_2Ln_2Ti_3O_{10}$ (Ln = La, Nd) using methylamine, *n*-butylamine, monoethanolamine and methanol as organic components. Possibility of the hybrids synthesis is studied in a wide range of conditions using both standard laboratory techniques and solvothermal/solvothermal-microwave methods. Suitable ways of producing single-phase inorganic-organic derivatives are established. Characterization of the products is performed with an emphasis on their structure, composition, thermal stability and morphology.

**Acknowledgements.** This research was supported by RFBR (grants № 16-33-60082 and № 18-03-00915). Authors also are grateful to State University Research Park: Center for X-ray Diffraction Studies, Center for Chemical Analysis and Materials Research, Center for Thermal Analysis and Calorimetry, Center for Nanotechnology.

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# Synthesis and exfoliation of layered perovskite-like titanates $HLnTiO_4$ and $H_2Ln_2Ti_3O_{10}$ intercalated by amines (Ln = La, Nd)

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Protonated layered perovskite-like oxides are solid crystalline substances in which two-dimensional nanosized perovskite slabs alternate with interlayer spaces containing protons. Being solid acids, these compounds are able to react with organic bases giving non-covalent inorganic-organic hybrids – substances consisting of ionically bonded inorganic and organic parts in which the inorganic part serves as a spatial frame [1]. Intercalation of organic bases into the interlayer space is accompanied by an increase in the interlayer distance proportional to their size and quantity. Due to this, the hybrids may be exfoliated into monolayers – separate perovskite slabs with high specific surface area and small thickness, which may be used as catalysts and photocatalysts owing to effective reagents adsorption and decrease effect of volume electron-hole pairs recombination, that's increase the photocatalytic reaction rate [2]. However, inorganic-organic hybrids based on layered perovskite-like titanates and their exfoliation ability are not sufficiently studied.

The present work is devoted to synthesis and exfoliation of inorganic-organic hybrids based on protonated titanates $HLnTiO_4$ and $H_2Ln_2Ti_3O_{10}$ (Ln = La, Nd) with amines as organic components. Characterization of the products is performed with an emphasis on their structure, composition, thermal stability and morphology. Particular attention is paid to selection of suitable exfoliation conditions and to increasing the completeness of the exfoliation.

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# Synthesis and Photophysical Properties of Cyclometalated Iridium(III) Complexes Based on Phenanthro[9,10-d]imidazole Ligands

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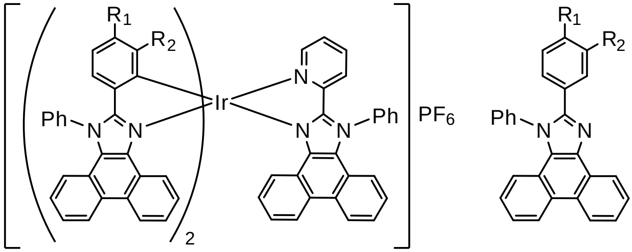
Cyclometalated iridium(III) complexes attract considerable attention due to their unique photophysical properties: high emission efficiency and long lifetime of the excited state. These compounds are widely used in OLED technologies, luminescent microscopy, bioimaging, and sensing [1].

Herein we report the synthesis and characterization of a series of novel Ir(III) complexes with polyaromatic imidazole-based ligands (Fig. 1).



**1**: $R_1$=$R_2$=H
**2**: $R_1$=H, $R_2$=Br
**3**: $R_1$=$NO_2$, $R_2$=H

*Fig. 1. Structures of the complexes and ligands under study.*

The compounds were characterized in solution by using NMR-spectroscopy and mass spectrometry and in solid state by X-ray diffraction analysis. Photophysical properties of both the C^N-ligands and the complexes were carefully studied. The complexes obtained display phosphorescence and sensitivity of their emission to molecular oxygen were evaluated. The data obtained allow estimating the influence of the ligand structure and donor properties onto the photophysical characteristics of the complexes.

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# Adsorption of iron (III) ion from aqueous solutions on porous glasses with different pore sizes

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Increased industrial has resulted in the generation of toxic pollutants. To avoid pollution of natural waters and subsequent metal accumulation in food chain, heavy metal ions should be removed from the source. Among many natural materials used for that purpose the high-silica porous materials has an important role. High-silica porous glasses (PGs), prepared through chemical leaching of alkali borosilicate glasses, have a wide range of pore sizes (from 0.3 nm up to 1000 nm), very high surface reactivity, low water solubility, stability under reducing and oxidizing conditions, availability and low cost.

The ability of the micro- and macroporous glasses (average pore radii 1.3 nm – MIP; 3.1 nm – MIP 750 $^0$C and 12.5 nm – MAP) to remove $Fe^{3+}$ from ferric chloride aqueous solution ($10^{-3}$ – $10^{-4}$ M; pH value of 3.0 ± 0.1) has been investigated.

PG samples (40 mg – MIP, 80 mg – MAP and 160 mg – MIP 750 $^0$C) were immersed in 40 sm$^3$ of solution with a preset concentration, and the obtained dispersions were left for 24 hours. After centrifugation, the iron (III) content in the solution before and after adsorption was determined by atomic absorption spectroscopy with inductively coupled plasma. The results for MAP glasses were compared with the results of adsorption on same glasses done in solutions for 30 minutes with stirring.

The present investigation showed that the removal efficiency of $Fe^{3+}$ decreases with the increase in initial $Fe^{3+}$ concentration. The adsorption values for the MAP glass do not depend on the time of contact between PG and electrolyte solution and maximum adsorption value in the monomolecular layer is equal to $3.4 \times 10^{-11}$ mol/cm$^2$. The experimental data yielded excellent adsorbent within the following order MAP > MIP > MIP 750 $^0$C based on its maximum value of the adsorption of the iron ion. The equilibrium data were analyzed using Langmuir and Freundlich isotherms.

The reported study was funded by RFBR according to the research projects № 17-03-01011 and № 18-03-01206. The studies were carried out using the equipment of the Interdisciplinary Resource Center in the direction "Nanotechnology" and the Center of Collective Use of Scientific Equipment of the Institute of Silicate Chemistry of the Russian Academy of Sciences.

# Sustainable diagnostics: photoactive $TiO_2$ instead of $H_2O_2$ in testing systems for visual and tactile diagnostics available to blind people

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Blind and color blind people can't afford colorimetric diagnostic; the problem is especially severe in rural areas were hot temperature and absence of electricity challenge modern diagnostics. Here we propose to replace the unstable component of a diagnostic test, $H_2O_2$ to stable dry $TiO_2$. Under UV irradiation, $TiO_2$ forms reactive oxygen species (ROS) that initiate polymerization of acrylamide causing liquid-to-gel transition in analyte –dependent manner. We demonstrate that specific DNA sequences can be detected by this approach. This development may enable detection of biological molecules by users with limited resources e.g. in developing countries or for travelers in remote areas.

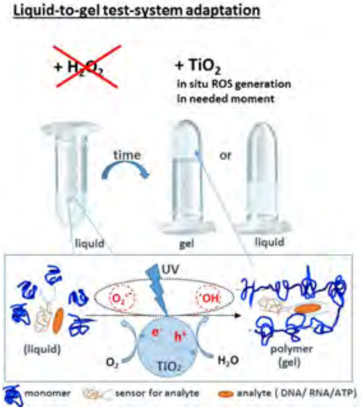

*Fig. 1. Schematic of i) photoreactions of formation of ROS on photoactive titania with photogenerated photohole ($h^+$) and photoelectron ($e^-$); ii) a portable sensor based on light-induced liquid-to-gel transition for polymer by radical polymerization on $TiO_2$ particles.*

**Acknowledgements.** This work was supported by the RSF grant no. 17-79-20186.

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# Layer-by-layer synthesis of new cathode materials based on ferrocyanides of transition metals

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Prussian blue and its analogues with different transition metals are an interesting class of compounds with a cubic structure. Atoms of transition metals presence in the structure and the possibility of changing the valence state of atoms determine the unique electrochemical, electrochromic, photophysical and magnetic properties [1]. The positive value of the reducing potential of $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ 0.36 V allows to use of ferrocyanides of transition metals as cathode materials for aqueous batteries.

The electrochemical characteristics of the cathode materials based on ferrocyanides of transition metals primarily depend on the particle size and the presence of water molecules and cations in the intercalation cavities [2]. The most popular way of obtaining of these particles with nanoscale is synthesis by co-precipitation in solution [3], which allows controlling the size of particles depending on the synthesis conditions. The disadvantage of the method is the need to stabilize nanoscale particles and the use of a conductive polymer for the manufacture of cathode material, which can reduce the cathode capacity due to the presence of electrochemically inactive components.

In this study, ferrocyanides of transition metal were synthesized by layer-by-layer synthesis directly on the conductive tin oxide support, fluorine-doped, in the form of a nanoscale film. Layer-by-layer assembly allows obtaining multifunctional nanocomposite coatings of a given thickness with the desired properties, structure and morphologies. The structure and morphology of the compounds were studied by X-ray diffraction analysis, scanning electron microscopy with energy dispersive X-Ray analysis and ATR-FTIR analysis. The effect of synthesis conditions (precursor of transition metals, number of cycles of layer deposition) on the particle morphology and the quality of the films obtained was shown. The electrochemical behavior of cathode materials was studied in a solution of magnesium salt by cyclic voltammetry.

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# Application of nonequilibrium thermodynamics to mass transfer modeling in pervaporation

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Membrane separation methods are introduced actively in the industry due to low energy consumption and environmental benignity of the process. Pervaporation, as one the methods, is based on vaporization through the membrane and allows to separate high boiling, thermally unstable, azeotropic mixtures. For improving the efficiency of the method, new materials are searched and theoretical concepts are developed.

The objects of the work are polymer membranes based on copolyimide P84 - (BTDA-TDI/MDI) {dianhydride 3,3'-4,4'-benzophenone tetracarboxylic acid and two diamines: meta-phenylenediamine (80%) and diaminodiphenylmethane (20%)} modified with nanoparticles of endometallofullerene Fe@$C_{60}$:

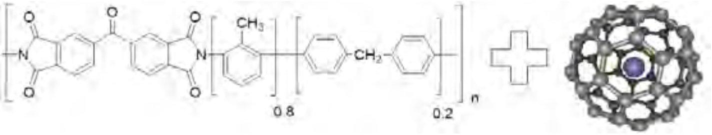

*Fig. 1. Chemical structure of copolyimide P84 and Fe@$C_{60}$ particle.*

The structure and physico-chemical properties of membranes were investigated by scanning electron microscopy and thermomechanical tests. The P84/ Fe@$C_{60}$ membranes were used to separate methanol/methyl acetate mixture by pervaporation. A simultaneous enhancement in both the separation factor and the flux has been achieved by optimizing Fe@$C_{60}$ loading.

Nonequilibrium thermodynamic was used to describe the mass transport of the components through membranes. Phenomenological coefficients $L_{kk}/L_{kl}$ were obtained and analyzed for pervaporation of the mixture in the range of methanol from 10 to 40 mol.% in the feed. The ratios of the activity coefficients of the vapors $\gamma_i$ to the composition of the liquid were set as NRTL (non-random two-liquid) functions with variable parameters $\tau_{12}$, $\tau_{21}$, $\alpha_{12}$. The received data showed high enough conformity of approximation curves and experimental results.

**Acknowledgments.** The investigation was carried out with financial support of Russian Science Foundation (RSF), grant 16-13-10164. Equipment of Resource Centers of St. Petersburg State University, namely, “Chemical Analysis and Materials Research Centre”, Interdisciplinary Resource Center “Nanotechnologies” and “Thermogravimetric and calorimetric methods of investigation” were used for investigation.

# Syntheses of cyclometalated platinum (II) complexes with alkynyl isocyanide ligands

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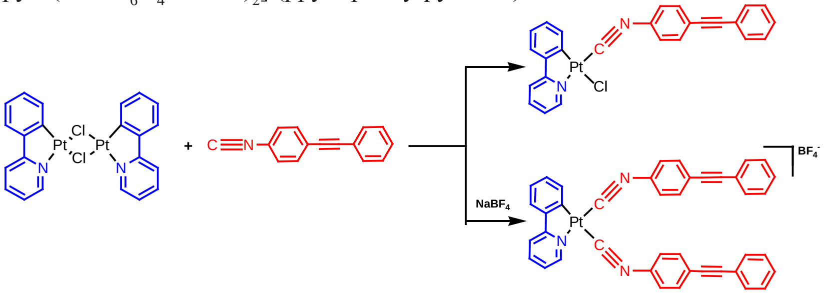
Nowadays, luminescent cyclometalated platinum (II) complexes are one of the most perspective materials for their potential applications in many fields, such as chemosensor, photocatalysts, light emitting diodes (LEDs), and photovoltaic devices. Emission from an isolated mononuclear platinum (II) complex is typically assigns to ligand centered (LC) and/or metal-to-ligand charge transfer (MLCT) states [1].

The introducing auxiliary ligands such as isocyanides in platinum (II) complexes provides fine-tuning of photophysical properties. The isocyanide fragment affords stabilize the lower oxidation states of transition-metal based on their strong σ-donor and π-acceptor properties. Moreover, these ligands extend the conjugation of the molecular system that promotes electronic communication and intramolecular charge/energy transfer (LC) between the connected components, opening a pathway to metal-based materials with attractive characteristics. In particular, isocyanide complexes of metals have been extensively employed to prepare and study different heteronuclear isocyanide arrays, exhibiting unusual structures with fascinating photophysical properties.

As part of the directional creation of luminescent materials based on cyclomelated complexes platinum (II) with multifunctional isocyanide ligands there were synthesized platinum complexes [ppyPt(C≡N$C_6H_4$C≡CPh)Cl] and [ppyPt(C≡N$C_6H_4$C≡CPh)$_2$] (ppy – phenylpyridine).



Structure of received compounds was identified by variable physical-chemical methods including IR spectroscopy, $^1$H, $^{13}$C{$^1$H} NMR spectroscopy and X-ray analysis.

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# Liquid-liquid equilibrium data for the systems ethanol – ethyl propionate – DES, propanol – propyl propionate – DES, butanol – butyl propionate – DES

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Today chemistry is actively looking for suitable substitutes of organic solvents due to its inherent toxicity and high volatility, which leads to air emission of volatile organic substances. First step in solving that problem was ionic liquids (ILs) being investigated for last two decades. Nevertheless, using of ILs is challenged because of its non-ecological characteristics like poor biodegradability, biocompatibility and sustainability [1]. Role of next generation in this area is presumably played by deep eutectic solvents (DES). DES is a eutectic mixture of two high-melting-point components with hydrogen-bonding interaction. DESs suppose new possibilities for designing of a task-specific solvent [2].

Herein DESs made from choline chloride in combination with glycerin and urea were taken for separation azeotropic mixtures of propanol, ethanol, butanol and corresponding propanoate esters. Tie-lines were obtained at temperatures 293.15, 313.15 K and atmospheric pressure. The compositions of coexisting organic and DES phases are determined by NMR-spectroscopy and gas chromatography. The extraction performance was characterized with distribution coefficients and values of selectivity for ethanol, propanol and butanol.

**Acknowledgements.** This study was supported by the Russian Foundation for Basic Research (project no. 16-33-60128). The experimental work was facilitated by the equipment of Magnetic Resonance Research Centre at St. Petersburg State University.

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# Synthesis of 3-aryl-1*H*-benzo[4,5]thieno[3,2-*b*]pyrroles as precursors of BODIPY dyes

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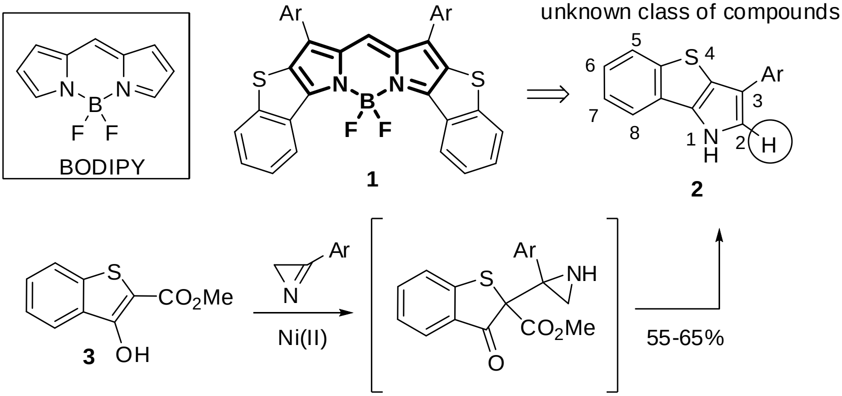
Boron–dipyrromethene (BODIPY) fluorescent dyes are widely used due to their high quantum yield, intense absorption and tunable emission wavelength. The ongoing search for new BODIPYs with improved fluorescent properties involves, synthesis of various fused boron–dipyrromethenes and, in particular, 1*H*-benzo[4,5] furo- and thieno[3,2-b]pyrrole derivatives [1]. The latter system (compound **1**) can be synthesized from 2-unsubstituted 1*H*-benzo[4,5]thieno[3,2-b]pyrroles **2**, which, however, still remains unknown compounds.

In this work we developed a method for the preparation of 2-unsusbstituted 3-aryl-1*H*-benzo[4,5]thieno[3,2-*b*]pyrrole derivatives using the annulation reaction of 3-hydroxybenzothiophene-2-carboxylates **3** with 3-aryl-2*H*-azirines. The reaction proceeds under Ni(II)-catalysis providing good yields of thienopyrroles **2**. The unusual mechanism of the reaction is discussed.



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# Direct determination of fluorine in KTP crystals by time-of-flight mass spectrometry with pulsed glow discharge in neon

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In the 20th century many of fluorine-containing compounds plays an important role in different fields [1] . For example, the crystals of potassium titanyl phosphate $KTiOPO_4$ (KTP) is a most commonly employed nonlinear material. When doped with fluorine, this material finds out the substantially increased radiation strength due to reducing the formation rate of colouring centers. However, fluorine quantification in any water insoluble matrices poses a serious analytical challenge for both ‘wet chemistry’ techniques and direct methods.

This study is devoted to the development of a new approach to the quantitative determination of fluorine in dielectric crystals using pulsed glow discharge time-of-flight mass spectrometry (PGD TOF MS). Combined Hollow Cathode (CHC) was used as a discharge cell. Different plasma gases including argon [2], argon-hydrogen mixture, and neon were considered. The following parameters were optimised: repelling pulse delay, discharge duration, voltage and pressure of the discharge cell. It was found, that in neon plasma fluorine, unlike the other constituent elements of KTP crystal - phosphorus and potassium, is ionised by high electron ionisation at short repelling pulse delay times. The use of neon as a discharge gas for elemental analysis of KTP crystals increased the sensitivity of fluorine determination by several times, in comparison with the argon glow discharge, and significantly reduced its detection limit. On the other hand, the sensitivity of the other constituent elements of KTP were significantly decreased, and the detection limits were correspondingly increased, so it is better to use argon-hydrogen plasma for their determination. However, the detection limits for K, P, Ti, and O, in neon plasma are enough for the nonstoichiometry control.

**Acknowledgements**.The research was carried out at the expense of the Russian Science Foundation grant (project No. 17-73-20089).

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# Cycloaddition of cumulated cycloalcadienes with nitrones

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The Isoxalidines are utilize for the synthesis of various alkaloids, for example, derivatives based on pyrrolizidine, quinolizidine, indolizidine and tropane [1]. In addition, substituted isoxazolidines can exhibit antitumor, antiviral and antibacterial activity [2]. Now, the reactions of nitrones with allenes that are activate by acceptor groups (ester, sulfones group) are the most studied. Previously, our research team has conducted studies on interaction of 1,3-dipoles with unactivated allenes (N-propadienyindole [3], arylallenes [4]). The interaction of nitrones with cyclic allenes has not been research previously.

In the course of our ongoing research, reactions of 1,2-cyclononanediene and 1,3-dipoles (ketonitrones and aldonitrones) were studied (Fig. 1).

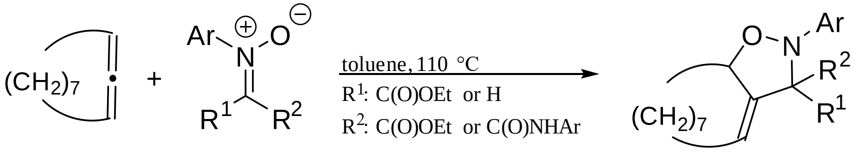

*Fig. 1. General view of the reaction of the interaction of allenes and nitrones.*

It was found that the 1,3-dipolar cycloaddition regioselectively, with the formation of 4-methyleneisoxazolidines. The reaction with aldonitrones goes with the formation of two stereoisomers. Based on the study of NMR-spectra of products (including HSQC, HMBC and NOESY), cis-configuration has been prescribed for the major isomers. All adduct was obtained with good yields.

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# Chemical equilibrium and vapor - liquid equilibrium in the system with ethyl acetate synthesis at 40˚C

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Data on chemical and phase equilibria in systems with chemical reactions are of interest for the organization of technological processes involving reacting mixtures. One of the most important types of combined processes of chemical technology is reaction rectification [1, 2]. Development of new effective methods of organization of reactive distillation process requires the development of an experimental database. Currently, the most studied are chemical equilibrium and vapor-liquid equilibrium in systems with the synthesis of carboxylic acids esters. This is due to the practical significance of the production of these products. Nevertheless, experimental data on combined processes are lacking even for the above systems: the available database should be also augmented for advancing the fundamental theory of complex equilibria [3].

This report presents data on the chemical equilibrium in the system with the ethyl acetate synthesis reaction and model calculation of the equilibrium between chemically equilibrium solutions and their vapor at 40˚C.

**Acknowledgements.** Authors acknowledge Resource Center of Saint Petersburg State University "Chemistry Educational Centre". Alexandra Golikova is grateful for the scholarship of President of Russian Federation (SP-2680.2018.1).

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# Feasibility study of urine elemental analysis as a way for prostate cancer diagnosis

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Prostate cancer (PCa) is one of the leading causes of cancer mortality in males. According to the statistics of American Cancer Society, about 1 man in 9 will be diagnosed with prostate cancer during his lifetime [1] .Significant improvement of patient survival rates is impossible without appropriate methods of early PCa detection. Nowadays two most common tools, applied for this purpose, are the test for prostate specific antigen (PSA) and digital rectal exam. The PSA test is known to have quite low sensitivity and specificity [2]. This is explained by the fact that high level of PSA is not necessarily associated with prostate cancer and might be caused by other pathological processes. Currently the prostate biopsy is a golden standard of PCa diagnostics.

It is evident that the development of new non-invasive tools for PCa diagnostics is of great interest. Urine contains a multitude of potential PCa biomarkers [3], such as proteins, amino acids, or different volatile compounds. Concentration of chemical elements and especially their ratios are also supposed to be significant for the PCa diagnosis [4].

In this work we performed urine elemental analysis to discover if there are statistically significant differences in urine samples of patients diagnosed with PCa and healthy volunteers. The concentrations of 15 elements (Al, B, Ca, Cd, Fe, K, Mg, Mn, Na, P, Pb, S, Si, Sr, Zn) were measured by atomic absorption spectroscopy in urine samples of 32 patients diagnosed with PCa and 40 healthy volunteers. Moreover, all the possible concentration ratios were calculated. Various statistical methods including Wilcoxon test, principal component analysis, logistic regression and decision trees were applied for intensive data exploration. The results will be given in presentation.

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# Physico-chemical properties of the $C_{60}$-L-lysine derivative

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Water soluble derivatives of fullerenes is a perspective class of compounds due to possibilities of their application in various fields of science and technology especially in biology and medicine due to well-defined membranotrophic, cytoprotective, radioprotective, antioxidant, antimicrobial, antiviral and transport properties [1, 2].

This work is devoted to physico-chemical investigation of water solutions of the $C_{60}$-L-lysine derivative — $C_{60}(C_6H_{14}N_2O_2)_2$ - isothermal and temperature dependences of densities, concentration dependence of the refractive index, specific and molar conductivities, size distribution in water as well as to investigation of solubility in the $C_{60}$-L-lys-water binary system.

Physico-chemical properties of the $C_{60}$-Lys water solutions were investigated. The concentration dependence of density was investigated by the pycnometer method; the average molar and partial volumes of the solution components were calculated at 298.15 K. By the isothermal saturation method the temperature dependence of solubility in $C_{60}$-Lys – water binary system was studied. Temperature dependences of the $C_{60}$-Lys solubility and density in water shown the following: the $C_{60}$-Lys derivative is rather well-soluble in water ($10\ g\cdot dm^{-3}$); the diagram of solubility consists of two branches corresponding to solubility of crystallohydrate $C_{60}(C_6H_{14}N_2O_2)_2\cdot 5H_2O$ (low-temperature branch) and non-hydrated fullerene derivative $C_{60}(C_6H_{13}N_2O_2)_2$ (high-temperature branch). The specific and molar conductivities, dissociation constant and apparent degree of dissociation were calculated for the $C_{60}$-Lys water solutions. By the dynamic light scattering method, the average size of the $C_{60}$-Lys associates was determined. The urgency of such investigation is close It should be noted that calculation of concentration dependence of $pK_D$ is conventional because the C60-Lys particles exist in solution in the form of large colloid species. Thus the amino acid moieties may be hidden from water and the real number of the ionizing groups is lower than the formal molar concentrationly connected with possibilities of application of the obtained results for the development and optimization of the water-soluble derivatives of fullerenes with amino acids application in biology and medicine.

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# Interaction of tetrazole-containing palladium(II) and platinum(II) complexes with DNA

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Anticancer agents based on the platinum metals complexes are widely used in malignancies therapy [1]. An introduction of various heterocyclic ligands (phenanthroline, imidazole, pyrimidine, purine, etc.) in the structure of the complexes is a perspective approach in developing of new platinum group metals-based drugs with improved efficiency and few side effects is [2]. Tetrazole-containing coordination compounds of the metal ions are known as promising compounds exhibiting antitumor activity.

In a series of papers it was reported that Pd(II) and Pt(II) complexes featuring tetrazole ligands are among the perspective compounds. Palladium(II) and platinum (II) complexes *trans*-$[MCl_2L_2]$ {M = Pt, Pd; L = 5-methyl-1H-tetrazol-1 -ylacetamides} were synthesized and characterized by HRESI$^+$-MS, $^1$H, $^{13}$C{$^1$H}, $^{195}$Pt NMR and IR spectroscopies. A binding of the complexes to calf-thymus DNA (CT DNA) were studied by means of UV technique. According to the spectroscopic data, the interaction of the metal complexes with CT DNA is confirmed. A significant increase of the melting point of CT DNA in the presence of the metal complexes ($\Delta T_m$ = 10.0°C) indicates a strong stabilization of structure.

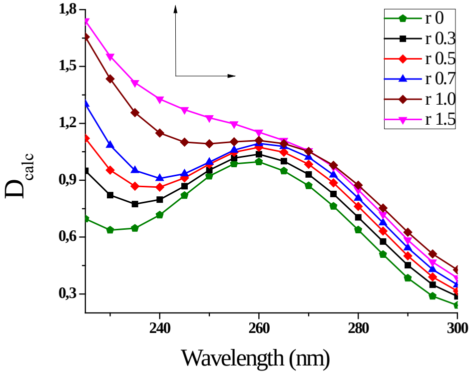

*Fig. 1. Calculated absorption spectra of CT DNA solutions in 5 mM NaCl with different concentrations of complex **1b.***

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# Thermodynamic aspects of chemical and technological processes in pulp industry on the example of a system containing amyl acetate

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The investigation of phase equilibria in different multicomponent systems is one of the promising ways in current scientific research. The interest to this aspect of thermodynamics is caused by wide use of such systems in technological processes in lots of industrial sectors.

Beyond that, investigating of critical states is becoming more and more relevant today. The interest to this phenomenon is caused by the fact that in critical (plate) points systems can exhibit new properties which do not occur in other states [1,2].

The objects of our investigation are ternary systems acetic acid-amyl alcohol-water, acetic acid-amyl acetate-water, amyl alcohol-amyl acetate-water and a quaternary system amyl acetate-amyl alcohol-acetic acid-water at 318,15 K. These systems attract interest due to the fact, that systems containing amyl acetate are important for pulp industry owing to use of amyl acetate as the solvent of cellulose and its derivatives.

The method of studying phase equilibria, solubility and critical points in our systems is cloud point technique in isothermal and isobaric conditions. Acquired data was processed using Gibbs-Rosebom triangle and Cartesian coordinate system in order to obtain information about form of binodal and to know the location of plate point. Knowing the form of binodal was important to us, because we tried to get the equation for that curve depending on equation of phase equilibrium and condition of phase equilibrium stability.

**Acknowledgements.** Maria Toikka is grateful for the scholarship of President of Russian Federation (SP-2140.2016.1).

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# Determination of hydrophobic bioactive analytes in complex matrixes by microemulsion electrokinetic chromatography (MEEKC) using imidazolium ionic liquids

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Electrokinetic chromatography in both modes (micellar; MEKC) and microemulsion (MEEKC)) is a good alternative for capillary zone electrophoresis for separation of wide range of compounds. Interest in ILs used as separation media in capillary electromigration methods is due to the fact that they can provide an alternative separation mechanism. It is of great interest to investigate the possibilities of different ionic liquids (ILs) as modifiers of the electrophoretic system under the conditions of the MEKC and MEEKC and in on-line preconcentration techniques. The variety of combinations of cations and anions makes it possible to change the hydrophobicity of ILs and to use them both as a micelle and microemulsion-forming agent. Recently the great potential of ILs based on imidazole as modifies micelles for on-line concentration of ionogenic and neutral analytes (steroids, biogenic amines) have been shown in MEKC. We have investigated the possibilities of hydrophilic ILs based on imidazole ($C_{12}$MImCl, $C_{16}$MImCl) as modifiers of electrophoretic system for the separation of steroids and polyphenols in MEEKC. The influence of ILs concentration, the nature and pH of the background electrolyte (BGE), the ratio of the components of micellar and microemulsion to the efficiency and selectivity of their separation were studied. Sufficient increase in resolution has been achieved by addition of (2-hydroxypropyl)-β-cyclodextrin into the BGE. The obtained results were compared with the use of a traditional cationic surfactant, cetyltrimethylammonium bromide. The sensitivity in capillary electrophoresis is often insufficient for the low concentrations of analytes in real samples. Different variants of on-line sample concentration, such as stacking and sweeping have been studied using ILs to improve the detection sensitivity of analytes by MEEKC.

**Acknowledgements**. This work was supported financially by grant of Russian Foundation for Basic Research no 16-03-00791-a and 17-03-01282-a. Authors thank Chemistry Educational Centre of Research Park of Saint-Petersburg State University for technical support.

# Deep eutectic solvents based on chloride choline as entrainer for the separation alcohol–ester systems

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In the last three decades, the concept "green" acquired a new significance in chemistry. The definition of sustainable development and green chemistry changed the way of thinking in process and chemical engineering. In this context, minimizing the environmental impact of solvents used in chemical production became a prior target. New approaches were taken toward the use of safer alternatives with more environmentally friendly properties. Example are the use of "biosolvents" produced from readily available renewable resources and the use of ionic liquids (ILs) with negligible vapor pressure and no potential emissions to the atmosphere. Recently, many studies concerning the environmental impact of ILs have shown that despite their unique properties and clear advantages in an ever-wide range of applications and processes, ILs are not intrinsically green. In a search for biodegradable and low toxicity, a new type of ILs has been developed, the deep eutectic solvents (DESs). DES are defined as a mixture of two or more components, which may be solid or liquid and that at a particular composition present a high melting point depression. They are much cheaper than IL and could be easily synthesized from biodegradable components.

In the work presented here, the possibility of using chloride choline and oxalic acid based DES for alcohol-ester systems separation is presented. Liquid-liquid phase equilibrium for ethanol-ethyl propionate, n-propanol – n-propyl propionate and n-butanol – n-butyl propionate mixtures with DES at a temperatures of 313,15 and 323,15 K was explored. The compositions of coexisting organic and DES phases are determined by NMR and gas chromatography. On the basis of experimental data, distribution coefficient of alcohol and ester and alcohol selectivity were calculated and analyzed.

**Acknowledgements**. This study was supported by the Russian Foundation for Basic Research (project no. 16-33-60128 mol_a_dk). The experimental work was facilitated by the equipment of Magnetic Resonance Research Centre at St. Petersburg State University.

# $^1$H and $^{31}$P NMR study of cyclic heterodimers and heterotrimers of phosphinic/phosphoric acids formed in an aprotic solution

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Phosphorus acids can form different cyclic complexes in solutions by hydrogen bonding proton-accepting P−OH and proton-donating P=O groups. Individually dimethylphosphorus and diphenylphosphorus acids in aprotic solutions form cyclic dimers and cyclic trimers [1, 2].

In this work the composition, structure and stoichiometry of the complexes formed from a mixture of $(MeO)_2POOH$ and $(PhO)_2POOH$ were studied by $^1$H and $^{31}$P NMR spectroscopy in freonic gases ($CDF_3/CDF_2Cl$). It was established that the heterocmplexes of three types (Fig.1a) are formed in almost equal proportions. Only one cyclic heterodimer signal is ob served that characterizes there is double reversible proton transition. In general, the H-bonds in the cyclic heterocomplexes are stronger than bonds in individual self-associates (Fig. 1b).

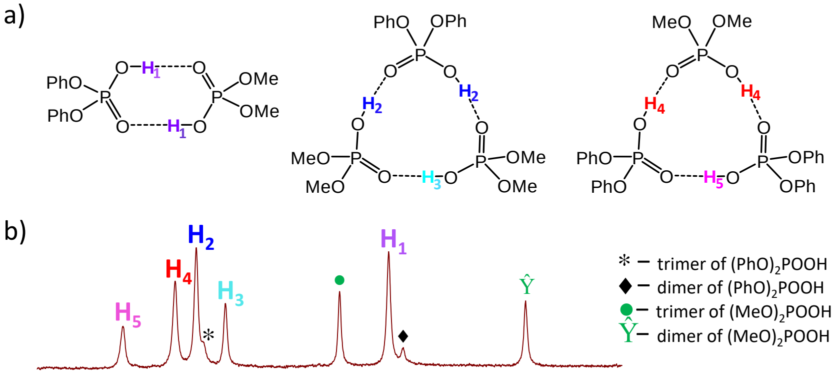

*Fig. 1. Structures of the heterodimer (a) and heterotrimers (b) of $(MeO)_2POOH$ and $(PhO)_2POOH$.*

**Acknowledgements**. This work has received financial support from the RFBR Grant 18-13-00050.

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# Optimization of Split Dapoxyl Aptamer for Real-Time Detection of Viral Infection

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Molecular diagnostics of viral infections relies on quantitative real-time PCR (qPCR), often in combination with fluorescently-labeled probes (e.g. Molecular beacon (MB) probe and TaqMan probe) for sequence-specific detection. However, qPCR technique requires expensive equipment and probes, as well as trained personnel, which makes qPCR-based diagnostics limited to specialized laboratories. For molecular diagnostics to be more affordable, isothermal amplification techniques are beneficial. For example, nucleic acid sequence based amplification (NASBA) is promising in the analysis of viral genomes. Most of the NASBA-based assays require downstream analysis of the amplicons (either by gel-electrophoresis or hybridization probes). Instantaneous real-time monitoring of NASBA amplicon using the MB probe was reported, but this probe requires two dyes to be conjugated to its opposite ends, and it suffers from high background.

Label-free probes are advantageous for cost-efficient nucleic acid analysis. Such probe can be based on light-up aptamers that bind a conditionally non-fluorescent dye thereby increasing its fluorescence. The RNA aptamers for malachite green and DFHBI (Spinach aptamer) are well known. Recently, a DNA aptamer recognizing dapoxyl dye has been selected (DAP-10) [1]. The advantage of DAP-10 over RNA aptamers is in its stability, which makes it a promising tool for real-time amplification assays.

Here, we report on optimization of a split dapoxyl aptamer (SDA) probe to be used in NASBA reaction for instantaneous monitoring of amplicon synthesis. The previously designed SDA probe [2] has the dye-binding module split into two halves, which are re-united once a specific nucleic acid target is bound. The original construct operates at 20-30 °C, but fails to report the target presence at 37-41 °C required for NASBA. We used a ration approach to modify a sequence of the SDA probe to work at the desired temperature. The optimized SDA constructs showed increased affinity to the dye only in the presence of the target. We demonstrated the use of the new generation of SDA probe for the detection of Zika virus RNA in NASBA reaction. Our results can be applied for the design of label-free probes for point-of-care diagnostics of viral infections, as well as for real-time RNA synthesis.

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# Pervaporation performance of polyamide membrane for desulphurization of n-heptane/thiophene mixture

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Pervaporation (PV) has recently gained much attention as an alternative or supplement for the conventional separation process for desulfurization of fuels in petrochemical industry. It is not only energy-saving and easy scale-up, but also allows separating azeotropic, close-boiling and thermally unstable mixtures. Various fuels have thiophene and heptanes in their composition, but thiophene along with other sulfur-containing compounds causes environmental pollution. Thus, the reduction of sulfur level in fuels is an relevant problem in the industry.

At present, the development of membrane materials with higher transport characteristic is one of the most challenging problem. Membranes based on polyamides are promising due to their high mechanical, thermal and chemical stability with appropriate separating properties.

The aim of the present work is an investigation of physico-chemical and transport characteristics of aromatic polyamide (PA) membrane.

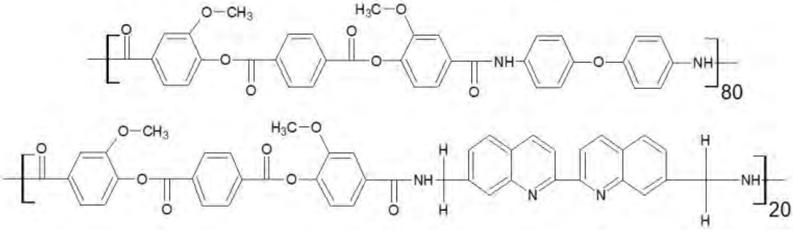

*Fig. 1. Scheme of PA.*

The PA membrane was characterized by thermogravimetric analysis, scanning electron microscopy and sorption experiments toward the components of the separating mixture. Transport properties were studied by pervaporation for organic sulfur removal. In this paper, n-heptane was chosen to simulate gasoline, with thiophene as the representative sulfur impurity. It was established that the membrane is selective to sulfur containing compounds and permeate preferably thiophene in pervaporation of thiophene- n-heptane mixture.

**Acknowledgments.** The reported study was funded by RFBR according to the research project № 18-33-01203. Equipment of Resource Centers of Saint Petersburg State University, namely, Interdisciplinary Resource Center "Nanotechnologies" and "Thermogravimetric and calorimetric methods of investigation" were used for investigation.

# Binuclear palladium diaminocarbene complexes for catalytic application

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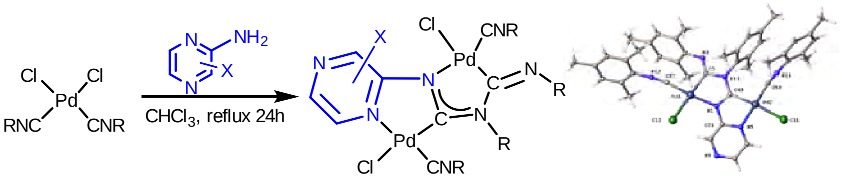
In the last decade acyclic diaminocarbene complexes (M-ADC) have been actively used in the catalysis of organic reactions that involve consecutive oxidative addition–reductive elimination steps [1]. In particular, Pd-ADC derivatives demonstrate outstanding performance in numerous cross-coupling reactions [2], while Pt-ADCs are efficient in hydrosilylation of alkynes. It has been recently reported that Pt-ADCs can be used as photocatalyst for hydrosilylation of alkynes under visible light irradiation [3].

In this study, we synthesized binuclear Pd–ADC complexes by coupling of palladium(II)-isonitrile complexes *cis*-$[PdCl_2(CNR)_2]$ with aminopirazines. Reactions were performed in chloroform at 60°C during 24 hours.



All obtained compounds were characterized by $^1H$, $^{13}C\{^1H\}$ NMR and IR spectroscopies, ESI$^+$-MS, elemental analyzes (CHN), and by X-ray diffraction.

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# Layer-by-layer polyelectrolyte capsules to modulate biofilms delayed fluorescence

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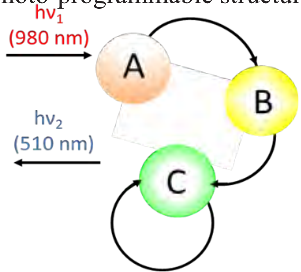
Nowadays scientific community knows many problems concerned biological systems. Such unsolved issues include targeted drug delivery, regulation of the cells' and tissues' behavior, development of systems for light conversion [1, 2].

The aim of our study was to develop a new strategy in the design of capsules based on titania core modified with silver nanoparticles and polyelectrolyte shells. L-arabinose was incorporated into the mesopores of the $TiO_2$ under vacuum. Then the polyelectrolyte shell was deposited on the $TiO_2$/Ag core. The obtained capsules were activated by IR-irradiation (λ =980 nm) and the L-arabinose release was 10 times faster than from inactivated capsules. The released L-arabinose switches the bacteria fluorescence which we monitor at 510 nm.

The proposed approach can be used in many applications where target and slow switching and light conversion is required. The obtained nanocapsules proved the possibility of developing photo-programmable structures for biological systems.



*Scheme 1. Signal processing in a biocompatible system. The system is activated by IR-irradiation. A – $TiO_2$/Ag/PE container initiator loaded with L-arabinose; B – L-arabinose releases from container and switch bacteria (C) illumination through interfering with the bacterial metabolic network; C - Escherichia coli XL-1 Blue pBAD-GFPuv (E. coli).*

**Acknowledgements**. This work was financially supported by the Russian Science Foundation (grant № 17-79-20186).

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# Development and study of PVA membranes modified by Pluronic F127

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Currently, among membrane methods the most promising and developing process for the separation of liquid mixtures is pervaporation which is environmentally friendly, energy-intensive and does not require large material costs. The development of pervaporation requires the search for new materials and the creation of highly efficient membranes on their basis. It can be achieved by the modification of polymeric membranes by organic nanoparticles. This component combination provides the best properties from both substances.

The aim of the present study was to improve the properties of the wide used polymer polyvinyl alcohol (PVA) by modification with Pluronic F127 (block copolymers of polyethylene glycol and polypropylene glycol) and to study the effect of Pluronic F127 introduction on the structure, physicochemical and transport properties of PVA membranes during pervaporation dehydration of water-organic mixtures. The optimal conditions for the preparation of composite PVA-Pluronic F127 membranes were developed. Structural and physicochemical properties of the membranes were studied by various methods of investigation (FTIR spectroscopy, scanning electron microscopy (SEM), swelling experiments and measurement of contact angles). The transport characteristics of obtained membranes were examined during pervaporation dehydration of industrially important solvents (ethanol, i-propanol) to evaluate the modification effect by Pluronic F127. It was shown that the introduction of Pluronic F127 into PVA matrix led to the improved transport characteristics of PVA membranes due to the significant changes of structure and morphology of the polymeric membranes.

**Acknowledgements**. This work was supported by Russian Foundation for Basic Research [grant No. 17-58-04067] and Belarussian Republican Foundation for Fundamental Research [grant No. X17PM-083]. The experimental work was facilitated by equipment from Resource Centers for Nanotechnology, Magnetic Resonance Research Centre, X-ray Diffraction Methods, Thermal Analysis and Calorimetry, Chemical Analysis and Materials Research Centre and GEOMODEL at St. Petersburg State University.

# Bulky substituted 2,2’-bipyridines as ligands for Cu(I) complexes design

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Substituted derivatives of 2,2’-bipyridine bearing electron withdrawing groups are attractive ligands for synthesis of Cu(I) complexes that potentially demonstrate unusual photophysical properties. Herein we report about investigation of reactivity of substituted 2,2’-bipyridines (Fig. 1) toward to Cu(I).

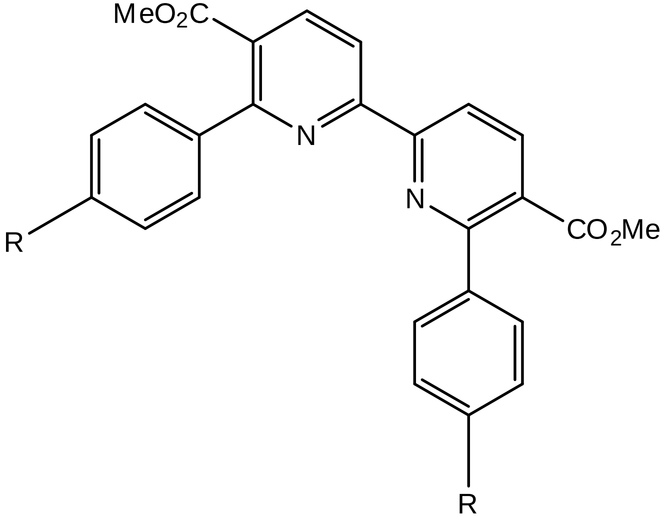

*Fig. 1. Substituted 2,2’-bipyridine, R=H, Cl, F.*

It has been found that attempt to prepare a heteroleptic phosphine-diimine Cu(I) complexes with cis-1,2-bis(diphenylphosphinoethylene) results in two homoleptic complexes $[Cu(NN)_2]^+$ and $[Cu(PP)_2]^+$ formation. After changing the phosphine ligand for 4,5-Bis(diphenylphosphino)-9,9-dimethylxanthene heteroleptic complex $[Cu(NN)(PP)]^+$ has been formed. All compounds obtained were characterized by polynuclear NMR spectroscopy and ESI mass spectrometry. Optical and photophysical properties of the complexes are investigated.

**Acknowledgements**. The authors greatly appreciate financial support from the Russian Science Foundation, grant 16-13-10064. The work was carried out using equipment of Centres for Magnetic Resonance, for Optical and Laser Materials Research, for Chemical Analysis and Materials Research, and X-ray Diffraction Centres (Research Park of St. Petersburg State University).

# Optically active inorganic nanoparticles for design of hybrid materials

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The production of new scleroprotein-based hybrid materials is very promising, since these objects are natural efficient and functional models of durable and lightweight systems that can work in virtually any environment [1]. The design of silk proteins based hybrids using the inorganic phase induction allows introduce new material properties. Due to their biocompatibility, these nanocomposites are promising in the field of tissue regeneration, targeted drug delivery, biosensors and bio-imaging [2]. Such innovative composite materials provide analogies to more conventional synthetic polymers, but with enhanced utility due to superior mechanical properties, biodegradability and functionalization. In the present work, the use of colloidal systems of optically active $HfO_2$ and $ZrO_2$ nanoparticles for spider silk based materials is highlighted.

Curtain-web spiders (genus Linothele Fallax) supplied the scleroproteins of the web fibers. $HfO_2$ and $ZrO_2$ nanoparticles were obtained by sol-gel method using controlled hydrolysis. The obtained nanoparticles and composite materials on their basis were characterized using the complex of physical-chemical methods. The hybrids revealed an optical upconversion response. (Fig. 1).

The work was supported by Russian Science Foundation, Grant No.18-79-00269.

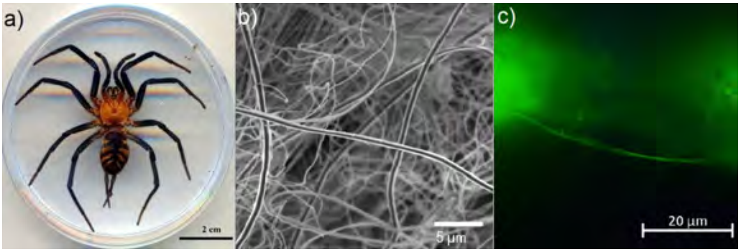

*Fig. 1. a) Linothele Fallax spider image; b) SEM image of hybrid material; c) Photoluminescence image of hybrid material.*

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# Cyclometalated Iridium(III) Complexes with Dialkylcyanamide Ligands

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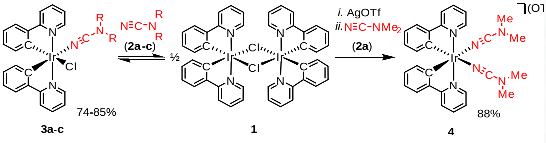
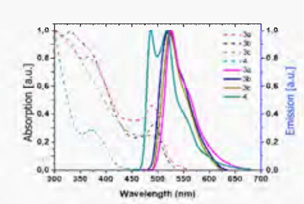
Transition metal dialkylcyanamide complexes attract significant attention for the past decades due to structural features of $NCNAlk_2$ ligands, which is differ from those of conventional nitrile ligands NCR (R = Alk, Ar) [1]. Within platinum group metal complexes, $(NCNR_2)M$ species are known for Ru, Os and Pt centers [1,2]. Therefore, synthesis and studies of iridium complexes bearing dialkylcyanamide ligands should fill the gap in the chemistry of these complexes.

In this work we have synthesized new *mono*- and *bis*dialkylcyanamide cyclometalated iridium(III) complexes $[Ir(ppy)_2Cl(NCNR_2)]$ [R = Me **3a**, Et **3b**, ½$C_5H_{10}$ **3c**] and $[Ir(ppy)_2(NCNMe_2)_2](OTf)$ (**4**) (ppy = 2-phenylpyridinato-*C*$^2$,*N*). The complexes **3a–c** was generated *via* the reaction of the chloro-bridged dimer $[Ir_2(ppy)_4(\mu\text{-}Cl)_2]$ (**1**) with 10-fold excess of the corresponding dialkylcyanamides (**2a–c**) in $CH_2Cl_2$ at RT (yields 74–85%). The *bis*dialkylcyanamide complex (**4**) was obtained by replacement of the chloride ligands with $NCNMe_2$ in **1** in the presence of AgOTf (yield 88%).





Complexes **3a**–**c**, **4** upon photoexcitation at 360 nm at 77 K exhibit luminescence with maximum emission at 522±2, 487 nm and an exponential damping time of 5 and 8 μs. The nature of Ir–N coordination bonds in **3a**–**c** were investigated theoretically using DFT calculations and AIM, NBO, and CDA methods.

**Acknowledgements**. This work has been supported by the Russian Science Foundation (grant 14-13-00060). Physicochemical measurements were performed at the Center for Magnetic Resonance, X-ray Diffraction Center, and Center for Chemical Analysis and Materials Research (all belong to Saint Petersburg State University Research Park).

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# Comparison of the methods for free Gibbs energy calculation for Mn(I) -catalysts

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The right choice of metal-based catalysts is the problem of interest in modern catalytic chemistry. Recently, catalysts on the base of Mn(I) have been developed due to their biocompatibility and low costs as the alternative for Pt, Pd and other noble metals. For example, non-pincer Mn(I)-catalysts demonstrate high efficacy in the reactions of esters hydrogenation [1].

One of the main properties of chemical reactions involved in the catalytic cycle is their free Gibbs energy, which allows predicting the possibility of the particular reaction. It can be calculated with *ab initio* quantum mechanics methods or can be estimated with the semi-empirical quantum mechanics or molecular mechanics methods. For high-throughput analysis of different pathways, it is very important to have fast but maybe not as exact methods. Molecular mechanics is the most suitable approach in this case, however, force field parametrization for Mn(I)-catalysts for such calculations still has not been obtained. Thus, the goal of this study is to define an appropriate force field parametrization for performing fast calculations of free Gibbs energy for Mn(I)-complexes participating in catalytic reactions.

As the first step in this work we consider semi-empirical quantum mechanics calculations of free Gibbs energy and its comparison with DFT method [2] for Mn(I)-based catalysts. We found that the results of semi-empirical calculations correlate well with the DFT ones in case of Mn(I)-complexes. For the small molecules, which also participate in the given catalytic cycle, correlation is not that high, but, in general, observed patterns may be also used in further studies using ReaxFF [3] and LAMMPS molecular mechanics software [4].

Overall, the obtained results mean that the semi-empirical approach can be used both on its own as a faster alternative to DFT and as a basis for defining parametrization of molecular mechanics methods.

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# The processes of self-organization in aqueous solutionsbased on cysteamine, mercapthopropionic acid and silver nitrate

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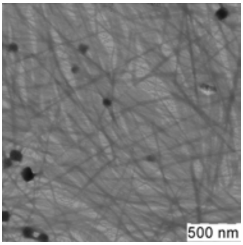

*Fig. 1. Micrograph of the sample CA – $AgNO_3$, molar ratio of components 1:1, $C_{AC}$ = $C_{AgNO3}$ = 3.0 mM.*

Hydrogels based on the aqueous solutions of L-cysteine (functional groups- SH,-$NH_2$, -COOH) and silver salts are of particular interest because a supramolecular gel- network is formed at a very low concentration of the dispersed phase (~0.01%) [1].

For a detailed elucidation of the mechanism of cluster formation, the set of studied systems should be expanded. For this aim we used various L-cysteine's derivatives - Cysteamine (CA) (functional groups –SH, -$NH_2$) and 3- Mercaptopropionic acid (MPA) (-SH, -COOH). The aim of the work was to clarify the possibility of formation of oligomeric chains and clusters and to investigate self-organization processes in aqueous solutions of CA, MPA and $AgNO_3$. The objects of the study are the solutions of the initial components (concentration - ~3.0 mM) at different molar ratio of 1:1 and 1:1.25 with addition 0.1 N KOH solution.

The structure of the systems and conditions of their formation were studied by means of different physico-chemical methods –UV, dynamic light scattering (DLS) – the measuring of particle size and ζ - potential, transmission electron microscopy (TEM).

It turned out by DLS that the formed aggregates are stable in time. The steady ζ-potential value of (MPA/Ag+ and Cysteamine/Ag+) at 1:1 and 1:1,25 was obtained and it was found that it has a positive charge. In the UV spectrum of systems absorption bands at 320-340 nm are observed, which may indicate the formation of silver–sulfur chains. Indeed, the TEM method confirmed visually this fact (Fig. 1).

**Acknowledgements**. The work was supported by the Ministry of Education and Science of the Russian Federation within the framework of the state works in the field of scientific activity (project No. 4.5508.2017/warhead) on equipment of collective use Center of Tver State University and Russian Foundation of Basic Research grant (project № 18-33-00146 mol_a).

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# New polyoxometalates including lanthanide ions as potential Luminescent Materials

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Low stability and extremely high cost of iridium compounds, which are used in organic light-emitting diodes, causes high importance of the search of new material in order to replace with them compounds that are used at the present time. Lanthanide complex compounds are promising in this area.

In the paper have been synthesized and studied new polyoxometalates are based on W-O-W clusters including Ti with doped ions Ln (Ln = Eu, Sm, Nd), as counterion are lithium ions. The resulting complexes have a luminescences (Fig. 1.) in a wide range of the spectrum and may be promising as potential luminescent materials.

Also these compounds, due to their special structure, are attracted scientific interest due their possible applications in medicine, as a universal enzyme inhibitors and antitumor agents [1-2].

*Fig. 1. Image luminescence complexes which include europium, samarium, neodymium.*

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# Thermodynamic and thermal properties of the $C_{60}(OH)_{24}$ derivative

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Water-soluble derivatives of fullerenes have potential for application in various fields of science and industry, for example as modifiers of natural and synthetic polymers, nanoionic materials, cements, lubricants and paints, as well as in biomedicine [1]. However, the number of papers devoted to the thermodynamic study of fullerenes and fullerene derivatives is scares.

Using precision adiabatic vacuum calorimetry, the isobaric heat capacity data for $C_{60}(OH)_{24}$ derivative in the temperature range T = 5 to 326 K were obtained (Fig. 1), as well as standard thermodynamic functions (molar third law entropy, standard molar entropy of formation) within a range of T = 5 to 326 K. The results of complex thermal analysis in the temperature range T = 303.62 to 1274.95 K (Fig. 2) show that the mass loss (in the temperature range 298 - 840 K) is equal to 36.51% and this value corresponds destruction of 24 hydroxyl groups.

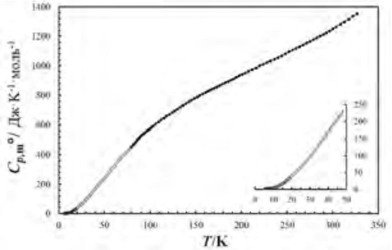

*Fig. 1. Temperature dependence of isobaric heat capacity of the $C_{60}(OH)_{24}$ derivative in the temperature range from T = 5 K to 326 K.*

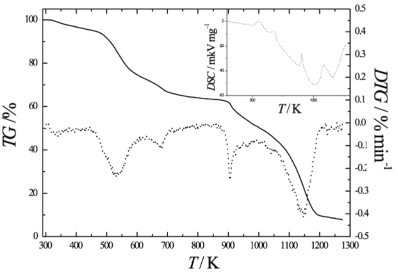

*Fig. 2. Complex thermal analysis of the $C_{60}(OH)_{24}$ derivative in the temperature range T = 303.62 to 1274.95 K. TG curve – solid line, DTG curve – dotted line.*

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# Liquid-liquid equilibrium for the quaternary system propionic acid - n-propanol - n-propyl propionate - water at 303.15 K

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The development of energy- and resource-saving ecologically clean processes is one of the main reasons for a detailed study of the physico-chemical properties of the combined processes in multicomponent reaction systems. Data of phase equilibrium are used for the optimization of such processes. However this scientific area is poorly researched, and most of the studies are represented by the results of studying the equilibrium of vapor-liquid systems, and information about liquid-liquid equilibrium, which is necessary in particular for replenishing the experimental data, is almost absent.

For considering phase equilibrium was taken the quaternary system propionic acid-propyl alcohol-propyl propionate-water. The choice of components is due to wide applicability each of them. Propyl propionate is the most important solvent, which used in the paint and varnish industry. Because of it's cheapness it can become a full-fledged substitute for the deficient butyl acetate. Propionic acid and it's derivatives and propyl alcohol are used in the production of herbicides, solvents, pharmaceutical preparations.

Determination the composition of the components in the system propionic acid-propyl alcohol-propyl propionate-water was carried out at 303.15 K and atmosphere pressure using gas chromatography. In experiment two ternary (propyl propionate-propionic acid-water, propyl propionate-propyl alcohol-water) and five quaternary systems which gross compositions corresponded to certain proportions of concentrations of propyl alcohol and propyl propionate (5:1, 2:1, 1:1, 2:1, 5:1) were analyzed. The initial proportions of the components in the system were determined using previously published data [1]. On the basis of the results obtained a binodal surface was constructed with a 3D concentration space. A comparative analysis of the experimental data with the literary [1] was carried out.

**Acknowledgements.** Maria Toikka is grateful to the Russian Science Foundation (grant 17-73-10290) for the support of this study.

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# Cu-doped $SnO_2$ nanoparticles: synthesis and functional properties

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Photochemical processes involved in various significant operations, such as water treatment and hydrogen energetics which have a great impact on our lives. The principal way to improve photochemical reaction is to use an effective catalyst and according to the literature n-type nanosized $SnO_2$ semiconductors are of great interest due to their wide band gap (Eg =3.6 eV). However, the impact of electronic structure on photodegradation effect is still under discussion.

The objective of this research was to study the correlation between the structure of as-prepared nanoparticles (NPs) and their functional properties. To clarify this aspect, we used Cu as a dopant for $SnO_2$ nanoparticles. The Cu : Sn molar ratio were varied from 12,5 to 50 : 100; the influence of pH values and initial reagent nature on NPs structure were also studied. Bare and doped $SnO_2$ NPs were obtained by the co-precipitation method. As expected XRD data demonstrated only rutile $SnO_2$ peaks (PDF 01-072-1147), the crystallite sizes increased for the higher pH values. According to TEM and SSA data, the nanoparticle size does not exceed 10 nm.

X-ray photoelectron spectroscopy confirms the presence of Cu in 2+ state. UV-vis absorption spectra show the difference between bare and Cu-doped $SnO_2$ nanoparticles. Besides, such parameters as Cu : Sn molar ratio and pH impacts on the estimated band gap and its values fallen up to 2.4 eV for a higher dopant concentration.

The obtained results were in a good accordance with impedance spectroscopy data. The conductivity vs temperature pattern for all the samples demonstrated the typical semiconductor behavior. The activation energy values increased from 3,73 eV for bare $SnO_2$ to 2,31 eV for Cu-doped (pH = 7, 50 : 100).

The dependence of kinetic of organic dyes photodegradation (Methylene blue, Congo red, Rhodamine 6G, 205-315 nm irradiation) and derivatives natures on NPs structures was also shown.

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# Nano-sized cation exchanger - stationary phase in capillary electrochromatography for aminoacids and catecholamines separation

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The advantage of using nanoparticles relies on their large surface-to-volume ratio and the availability of different surface functional groups. Nano-sized cation exchanger (NSCE) is promising material for electrophoretic separation of analytes due to its high ion-exchange capacity. Stable suspension of NSCE particles (styrene and 8% divinylbenzene copolymer matrix functionalized with sulfogroups) for the first time was obtained in [1] by two-step grinding of macro-sized ion exchanger followed by centrifugation. This work describes the application of NSCE as an ion-exchange stationary phase in capillary electrochromatography. It was established that introduction of NSCE in background electrolyte led to the modification of fused silica capillary inner walls. Formed physically-adsorbed coating turned out to be stable in a range of pH from 2 to 8. The characterization of the coating was also carried out by the scanning electron microscopy.

The prospects of obtained coating in the capillary electrochromatography mode for separation of catecholamines and aminoacids (biomarkers of various diseases) in cationic forms were considered. NSCE modified capillaries provided high efficiency ($N=330\text{-}520 * 10^3$ t.p./m) and selectivity of catecholamines and aminoacids during their electrophoretic separation due to sorption prevention. Besides, the on-line concentration techniques, such as field amplified sample stacking (FASS) and field amplified sample injection (FASI) were applied to decrease the detection limits. For instance, FASS provided 67-72 ng/ml and 72-625 ng/ml detectiom limits of catecholamines and aminoacids, correspondently. In case of FASI these values for catecholamines were even lower (6 – 7 ng/ml). Simultaneous application of NSCE-modified capillaries, sample preparation on aluminium oxide and on-line concentration techniques provided quantitative determination of catecholamines in urine.

**Acknowledgments.** The authors are thankful for the financial support provided by the RFBR (no. 17-03-01282_a and 18-33-01091 mol_a). Results were performed at the Interdisciplinary Resource Center for Nanotechnology and Chemistry Educational Center, Research Park, SPSU.

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# Palladium(II)-mediated coupling of mercaptoazoles with coordinated isocyanides

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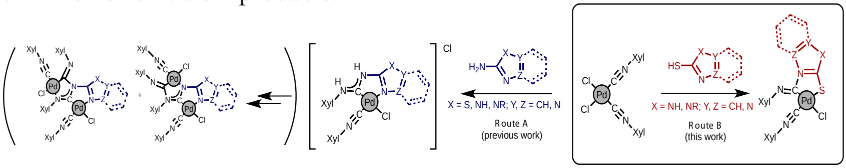
In recent decades, transition metal complexes with aminocarbene ligands (NHC - N-heterocyclic carbenes, ADC - acyclic diaminocarbenes) have taken a special place in coordination chemistry due to their wide application in catalysis, material design and medical chemistry. One of the promising and easy in processing methods for generating of complexes with various types of aminocarbene ligands is metal-mediated addition of nucleophiles to coordinated isocyanides.

Recently in our research group, it was found that the reaction of $Pd^{II}$ isocyanide complexes with ambident nucleophiles such as aminazoles leads to *C*,*N*-chelate carbene complexes, which themselves can act as a nucleophile and react with another moiety of the isocyanide complex, yielding binuclear products (Scheme 1, Route A) [1,2]. In the present work, we have studied the coupling of *bis*(xylisocyanide) $Pd^{II}$ complex with the another type of nucleophile – mercaptoazole (Scheme 1, Route B) leading to *C*,*S*-chelate carbene complexes which do not undergo to the formation of binuclear products.



*Scheme 1. Coupling of bis(xyllysocyanide) $Pd^{II}$ complex with amino- and mercaptoazoles.*

**Acknowledgements**. This work was supported by the Russian Foundation for Basic Research (grant 18-33-00704 mol_a). Physicochemical studies were carried out at the resource centers of St. Petersburg State University "Magnetic resonance imaging methods", "X-ray diffraction research methods" and "Methods for analyzing the composition of the substance."

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# Hybrid pervaporation membranes for the removal of sulfur containing impurities from hydrocarbons

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Membrane technologies are of special significance in solving the global industrial problems such as reduction of power consumption and non-waste production. Membrane process of pervaporation is among the most promising technical approach to separation and regeneration of valuable solvents, production of highly pure chemical substances, purification of waste water, and so on. Thus the development of novel membranes is one of the primary tasks.

The aim of present was searching membrane materials for desulfurization of industrial important media. Hybrid materials are perspective due to ability to combine benefits of both polymer and inorganic particles. In present work hybrid membranes were prepared by involving macromolecular stars with polymer arms of different nature in poly(2,6-dimethyl-1,4-phenylene oxide) matrix.

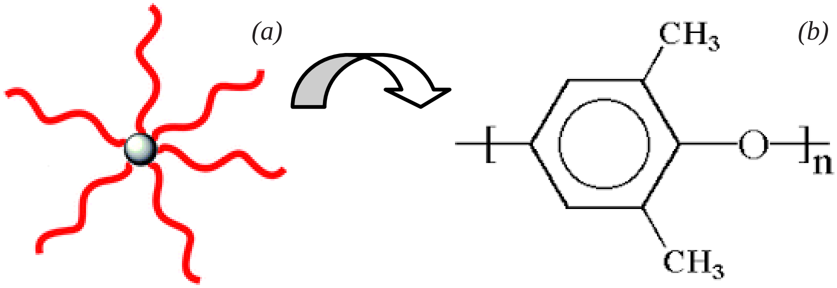

*Fig. 1. Macromolecular star (a) and polyphenylene oxide (b).*

The properties of developed materials were studied by TGA, X-ray diffraction analysis, density and contact angles measurements. Transport properties were investigated by pervaporation of sulfur containing n-octane as modeling mixture. N-octane is typically presented in gasoline. The reduction of sulfur content in transportation fuel should leading to the improved air quality. It was shown that hybrid membranes effectively remove sulfur containing impurities from n-octane and are perspective for industrial application.

**Acknowledgments.** The reported study was funded by RFBR according to the research project № 18-33-01203. Equipment of Resource Centers of Saint Petersburg State University, namely, Interdisciplinary Resource Center “Nanotechnologies” and “Thermogravimetric and calorimetric methods of investigation” were used for investigation.

# Solubility of hydroxyapatite in model solution of blood plasma (experiment and modelling)

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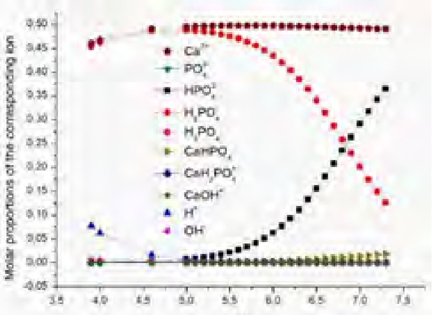
The solubility of hydroxyapatite has been the subject of extensive research for several decades. Biocompatibility of hydroxyapatite makes it promising for the development of artificial implants. Recently, researchers also pay attention at the phenomena of calcification of soft tissues.

Difficulties of study of hydroxyapatite solubility are due to slow setting of chemical and phase equilibria, and extremely low solubility. Even a small sampling can shift the equilibrium in the system. In this regard, it is important to provide a non-destructive analysis of the composition of a solution that is in contact with hydroxyapatite. Such analysis can be performed with membrane electrode selective to calcium ions, and the measurements can be done continuously, in real time, without sampling. The additional advantage of the method is that the sensor signal depends on the activity rather than the concentration of calcium ions in solution. It is the activity rather than the concentration determines the heterogeneous equilibria in solution.

In this study we have modelled the chemical equilibria in mixed solution: a prototype of the blood plasma, aimed at the study of calcification of tissues. The full set of equilibria including the dissociation of water and phosphoric acid, and formation of both inert and ionic calcium phosphates was considered. This allowed for the calculation of the concentrations (and by means of the Debye–Hückel theory also activities) of molecular–ionic forms containing calcium and hydrogen cations, and phosphate anions in the range of ionized-calcium and total phosphorus concentrations from 0.5 to 3.0 mM, and at the solution pH of 4.0–8.



The study was supported by the Russian Foundation for Basic Research (Grant No. 18-29-12114).

# Fabrication of stoichiometric and strictly oriented thin film of silver selenide using pulsed laser deposition

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The fabrication of silver selenide thin films attracts attention due to the possibility of utilizing them as IR-detectors, photovoltaic cells and magnetoresistive sensors. In addition, $Ag_2Se$ undergoes a transition to the superionic phase at the temperature of 135 °C.

Thin films with controlled thickness can be fabricated using pulsed laser deposition (PLD). However, all the previous authors reported a nonstoichiometric composition of silver selenide films produced by PLD [1]. The reasons for this deviation from the stoichiometry were investigated in the present work.

It was shown that selenium deficiency arises due to its re-evaporation from the surface of ablated particles. The addition of 20 at. % excess of selenium to the ablation target allows fabricating stoichiometric and strictly oriented (Fig. 1) thin film of silver selenide using PLD.

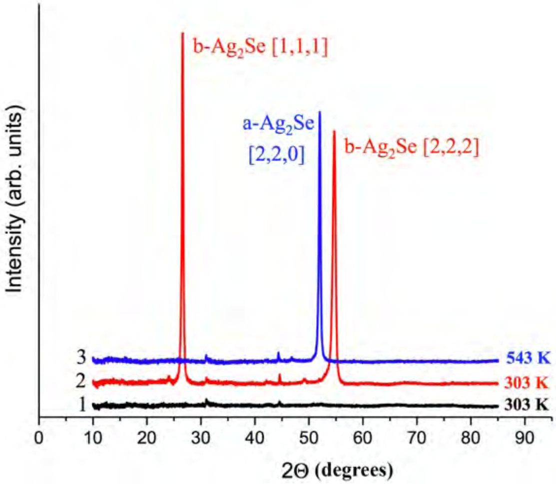

*Fig. 1. XRD patterns of the $Ag_2Se$ film deposited from a target with an excess of selenium after ablation (1), after annealing (2) and at the highest temperature during annealing (3).*

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# Synthesis of medium-sized rings by ox(thi)azepinone-fused hydrated imidazoline ring expansion (HIRE)

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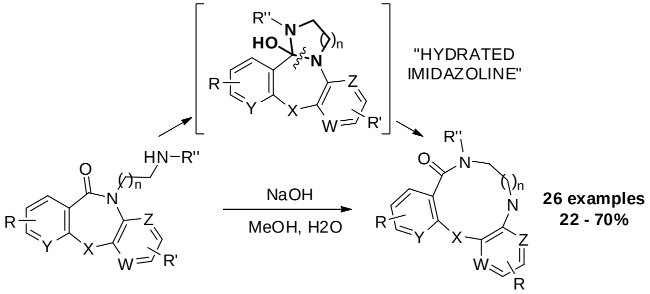
Compounds containing medium-sized rings have a significant potential in drug discovery [1,2]. Unfortunately, they are poorly represented in modern screening libraries due to the lack of efficient methods for their preparation [3,4]. Traditional end-to-end cyclisation reactions of linear precursors are typically inefficient, low-yielding processes. In contrast, the expansion of smaller ring systems is an attractive alternative to access medium-sized rings.

In this study, a novel synthetic methodology for assembly of medium-sized cyclic scaffolds was developed. We employed a hitherto undescribed ring expansion strategy involving expansion of thi(ox)azepinone-fused hydrated imidazoline (HIRE) for synthesis of 10-12 membered lactams.

The optimal expansion conditions were identified and the series of medium-sized ring containing compounds was obtained. In addition, the influence of the X atom and the length of aminoalkyl fragment on the conversion of the starting material in the HIRE reaction was investigated.



X = O, S, SO$_2$; Y,Z, W = CH or N; n = 1-3;
R = CH$_3$, Hal; R' = NO$_2$, CF$_3$, CN, SO$_2$N(CH$_3$)$_2$; R'' = H, -CH$_2$Ar(HetAr)

*Fig. 1. Scheme of Ox(thi)azepinone-fused hydrated imidazoline ring expansion (HIRE) reaction.*

This research was supported by the Russian Foundation for Basic Research (RFBR) (Project Grant 18-03-01081).

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# Assesment of acetylene-substituted aziridine as the key intermediate for the synthesis of porphyrin-fullerene assemblies

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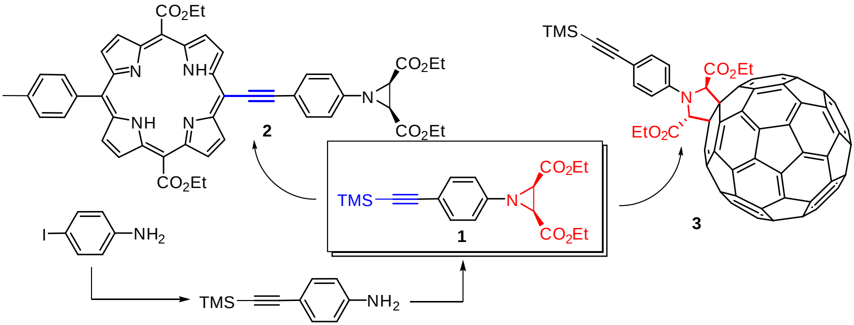
Porphyrin-fullerene dyads are a well-known class of molecules due to prospects of their implementation as solar energy conversion materials [1]. Photophysical properties demonstrated by these compounds greatly depend on their structure: both geometry and electron configuration of dyad can dramatically change them [2].

The present work is devoted to implementation of acetylene-containing aziridine **1** [3] in construction of novel porphyrin-fullerene dyads. Aziridine moiety of this “spacer-molecule” enables easy connection to fullerene by means of Prato reaction, while acetylene part allows linking it to the porphyrin moiety *via* Sonogashira coupling.



To assess the utility of the proposed building block, we synthesized TMS-protected acetylene substituted aziridine **1** in two steps from 4-iodoaniline, and developed the route towards unsymmetrical *meso*-brominated porphyrin. The coupling step leading to porphyrin **2** and cycloaddition step leading to fullerene **3** are discussed in the work.

This research was performed using resources of the Center for Magnetic Resonance, the Center for Chemical Analysis and Materials, the Educational Resource Center of Chemistry.

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# Luminescent ion-selective sensors based on the novel bipyridine-functionalized gold complexes

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Optodes are optical chemical sensors that respond to the analyte activity in the solution by changing their optical properties. They are miniature and easy to use devices. Their response is determined by the selective complexation of the ionic analyte with the active component occurring inside the optode phase.

We report here on our studies aimed at the investigation of the novel Au(I) complexes as promising candidates for application as active components in polymeric plasticized optodes. The complexes were synthesized in the laboratory of cluster compounds at St. Petersburg State University. They combine the luminescent organometallic moiety and the ion-selective part (phenylpyridine rings), Fig. 1A. The gold complexes I and II were The major problem of utilizing such compounds in complex matrix: luminescence quenching, was successfully overcome in this work (Fig. 1B).

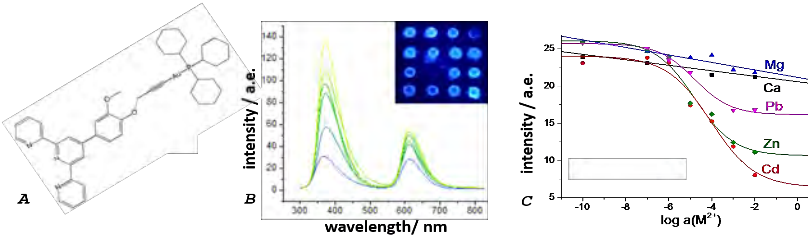

*Fig. 1. A: the structural formula of Au complex II; B: luminescent spectra of the optodes containing Au II in $Cd^{2+}$ solutions of different concentrations (UV-lamp illumination, 365 nm); C: dependence of the luminescence of Au II-based optode on the metal ion activity in the contacting solution.*

The response of the optodes containing gold complexes to the activity of $Ca^{2+}$, $Mg^{2+}$, $Zn^{2+}$, $Cd^{2+}$, $Pb^{2+}$ ions in the solution was studied (Fig. 1C). The highest sensitivity was observed for $Cd^{2+}$ and $Zn^{2+}$ cations.

As a result, we found it possible to develop polymeric optical sensors based on the novel organometallic complexes of Au(I) with preservation of the luminescence in the polymeric phase.

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# Laser-induced synthesis of metal/carbon nanoparticles with variable composition for complex biotoxic substances detection

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Metal/carbon hybrid nanoparticles demonstrate interesting optical effects associated with mutual influence of its chemical and physical interaction. The carbon component has good sorption properties, and surface plasmon resonance is observed in the metal phase [1]. This facilitates the use of nanoparticles in SERS spectroscopy.

The purpose of this work was to obtain hybrid Au-Ag@C nanoparticles through laser-induced synthesis with different Au/Ag ratio and to study their properties as amplifying matrices in SERS spectroscopy.

The composition of the samples was studied by EDX spectroscopy, the presence and characteristics of the plasmon resonance peak – by means of optical absorption spectroscopy.

In the course of the study, samples of nanoparticles with variable composition and peaks of plasmon resonance, were obtained. Fig. 1 shows the SEM photograph of the structures obtained.

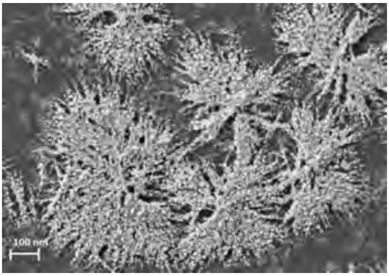

*Fig. 1. Photograph of SEM obtained hybrid Au–Ag@C nanoparticles.*

SEM photographs and EDX spectrum were obtained in the "Nanotechnology" Resource Center of St. Petersburg State University; optical absorption spectra were taken at the "Optical and laser methods for analyzing matter" RC of St. Petersburg State University. The work was performed within the framework of the RFBR project 17-03-01284 A “Hybrid metal/carbon nanostructures for detecting biotoxic substances of complex nature in environmental monitoring”.

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# Chemical equilibrium in the fluid system ethanol – formic acid – ethyl formate – water at 25°C and 35°C: experimental research and visualization

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Organization of industrial synthesis of esters requires detailed information on structure and features of phase diagrams of reacting systems, for example, data on mutual location of the solubility surface and the chemical equilibrium surface on phase diagram, since for industrial technologies of synthesis, initial concentrations of reagents are chosen in such a way to avoid undesirable phase transformations and to carry out synthesis in a homogeneous solution. The object of investigation was ethanol – formic acid – ethyl formate – water system with reaction of ethyl formate synthesis at 25°C and 35°C. Ethyl formate is an industrially important ester used, for example, in the production of paints and varnishes and polymer materials, in pharmaceutical and food industries. To study chemical equilibrium (CE), the method of nuclear magnetic resonance (NMR) was used. After reaching CE (about 10 hours) samples of equilibrium solutions were studied by $^1$H NMR spectroscopy using 500 MHz Buker AVANCE III NMR spectrometer to determine the compositions belonging to the surface of chemical equilibrium. The processing of the acquired spectra was carried out using MestReNova software. If the components of a solution under study and assignment of peaks on NMR spectrum are known, then it is possible to calculate molar fractions from the values of peaks' areas. After processing the spectra and determining the equilibrium compositions of solutions, the data were visualized using Origin 9.5 software, 3D surface of chemical equilibrium was presented in concentration tetrahedron. The data on chemical equilibrium were compared with the data on solubility, namely, location of the chemical equilibrium surface and the solubility surface in the concentration tetrahedron was analyzed: it was established that the surface of chemical equilibrium and the solubility surface do not intersect (at 25 and 35°C), which confirms the experimentally observed fact: the chemical equilibrium of the reaction of ethyl formate synthesis is achieved in a homogeneous region of compositions (positive trend for industrial synthesis of ester).

The study was carried out using the funds of grant of Russian Science Foundation (project No. 17-73-10127).

# Impact of surface composition of HAP nanoparticles on recovery value of toxic ions from water

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These days one of the relevant ecological problems appears to be a sewage treatment including removal of toxic metal ions. Presence of toxic metal ions in water causes damage to environment and affects health and existence of life forms. In this instance, it is vital to discover an optimal process of sewage treatment. Presently, purification of wastewater from these ions is produced by methods of precipitation or sorption. Recently special attention is paid to sorption method. Based on requirements, nanoparticles of hydroxylapatite (HAP) can be an optimal and perspective adsorbent. Furthermore, we propose to modify surface of HAP nanoparticles with polyethylene glycol (PEG) with different molecular weight as a bioinert modifier in order to discover the impact of surface.

The synthesis of unmodified nano-HAP particles and modified with PEG300 and PEG3000, was performed by precipitation method. Morphological characteristics were studied with XRD, TEM, BET method and FT-IR. For Cu2+, Co2+ and Ni2+ ions in certain amount of concentrations the adsorption equilibrium time and effect of the mass of nano-HAP for temperatures 25°C and 60°C were studied.

The conducted research shows that recovery value of Ni2+ ions for concentrations from 60 to 390 μg/ml was between was between 25 and 75% and had almost the same tendency for samples with various surface composition These values are quite satisfying and perspective. For Cu2+ ions recovery value was studied in concentrations from 50 to 500 μg. Nano-HAP showed high level of sorption for modified and unmodified HAP with low fluctuations, however, only for low concentrations. With rise of Cu2+ concentration recovery value decreases. Results of adsorption of Co2+ ions shows an extremely low level of recovery level, which demonstrate that HAP is inappropriate adsorbent in this case. All thermodynamical parameters were studied and showed in research.

**Acknowledgements.** Scientific research were performed at the Research Park of St. Petersburg State University educational resource center of chemistry: Centre for X-ray Diffraction Studies, Centre for Innovative Technologies of Composite Nanomaterials, Chemical Analysis and Materials Research Centre.

# Experimental study of phase equilibrium in quaternary reacting system propionic acid – ethanol – ethyl propionate – water at 20°C

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The study of phase equilibrium of reacting systems is a great interest not only for the development of fundamental thermodynamics, but also for applied science [1]. These data allow modernizing the technology of reactive mass-exchange processes, for example, esterification and extraction. However, despite the obvious scientific and applied importance of systems, the physico-chemical properties of which can be determined by the phase equilibrium, the available data are rather limited. Thus, the study of phase equilibrium is currently very important.

The work is devoted to the study of liquid-liquid equilibrium (LLE) in multicomponent reacting systems. In this paper, the propionic acid – ethanol – ethyl propionate – water system was considered at 20°C.

The experimental study of LLE was carried out by Gas chromatographic method analysis for analytical determination of phase compositions. Experimental data on the liquid-liquid equilibrium in two ternary systems (propionic acid-ethyl propionate-water and ethanol-ethyl propionate-water) and quaternary systems (propionic acid - ethanol - ethyl propionate -water) were obtained. The initial series of quaternary solutions were prepared with the keeping of concentration of constant ratio of propionic acid and ethanol that is 3:1, 2:1, 1:1, 1:2, 1:3. These compositions conveniently display the form of binodal surfaces in composition tetrahedron. The compositions of the solutions were chosen so that the compositions of the coexisting phases (tie-lines) lay evenly on the binodal curve. These set of new experimental data enable to present the binodal surface in composition tetrahedron. The compositions of the coexisting phases are in good agreement with the experimental data on solubility obtained earlier at the Department of Chemical Thermodynamics and Kinetics. The obtained data of the liquid-liquid equilibrium of the propionic acid – ethanol – ethyl propionate – water system will be used for further study of its thermodynamic properties.

**Acknowledgements**. Maria Toikka is grateful to the Russian Science Foundation (grant 17-73-10290) for the support of this study.

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# Static tensimetry method with membrane null-manometer in applying to the study of the Lewis acid/Lewis base equilibrium

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Static method with membrane null-manometer is the unique tensimetry method which allows measuring the total pressure; obtaining composition of saturated and unsaturated vapor above the individual substances. Static method permits directly measure the pressure in a closed system in a wide temperature range (up to 400-1100 °C, depending on the glass type). Moreover, besides vapor pressure - temperature dependence, static method with membrane null-manometer gives information about transformations which occur in the studied system. For instance, information about the reversible/irreversible character of the chemical process, the temperature of dissociation/decomposition of the compound can be obtained. Static method is the only tensimetry method which allows one to study equilibrium in the homogeneous gaseous systems. In addition, static method allows to determine the dissociation enthalpies of the donor–acceptor complexes in the gas phase [1-5].

In the present work the interaction between $(C_6F_5)_2BC_6H_2(C_6F_5)_3$ (Lewis acid) and pyridine (Lewis base) was investigated by static tensimetry method with membrane null-manometer. With an initial ratio of pyridine to Lewis acid 3:1, a strong donor-acceptor complex of 1:1 composition is formed. The donor-acceptor bond between the boron and nitrogen atoms is so strong that up to 150˚C the dissociation of the solid complex is not observed. With a further increase of temperature up to 180 ˚C, release of pentafluorobenzene and formation of polymeric material is observed, which is due to the activation of excess pyridine by the Lewis acid. This is confirmed by mass-spectrometry study of the gas phase and IR-spectroscopy of the solid state.

We express our gratitude to Kazakov I.V. for assistance in experiments and Dr. Marian Olaru for providing the sample of (C6F5)2BC6H2(C6F5)3. This work was supported by the Russian Science Foundation grant 18-13-00196.

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# Solubility and critical phenomena for the system propionic acid –ethanol – ethyl propionate – water system at 293.15 K

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The scientific research is devoted to the critical phenomena observed in systems that have both of chemical and phase transformations and the solubility of these systems [1]. The study of such systems supplements the general knowledge of thermodynamics and furthers the development of organic synthesis.

The object of investigation in this research is quaternary reacting system propionic acid – ethanol – ethyl propionate – water at 293.15 K and atmospheric pressure.

The study of critical phenomena and solubility in the propionic acid – ethyl alcohol – ethyl propionate - water system at 293.15 K was carried out by cloud-point technique method. The special thermostat was constructed. We used the cloud-point technique method to obtain experimental data. For the best presentation of the solubility surface, the initial compositions were chosen so that experimental points were regularly placed on the binodal surface. In the course of all studies of the critical area, a pale blue opalescence was observed.

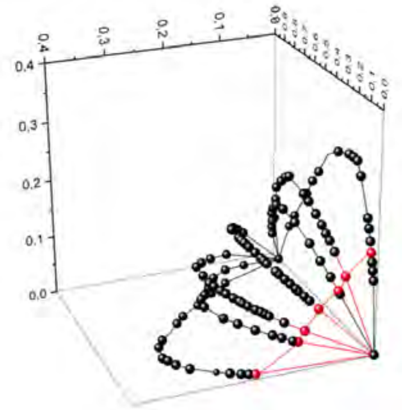

*Fig. 1. The binodal surface in system propionic acid – ethyl alcohol – ethyl propionate - water at 293.15 K.*

On the base of experimental results a solubility surface was constructed at 293.15 K (Fig. 1). The compositions of critical states were determined, and "critical curve" was constructed in the composition tetrahedron. The region of splitting is a relatively small area in the concentration tetrahedron; the overall concentration of ethanol and propionic acid on the binoof this study.

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# Choline chloride based deep eutectic solvents as extraction media for separation of azeotropic mixtures

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Nowadays, technical industries inevitably face the problems of environmental chemistry. The question of the need to use non-polluting chemical processes and reagents is becoming ever more acute. One of the first alternatives that classical solvents could replace were ionic liquids (IL). Ionic liquids belong to the so-called "green solvents", which correspond to the principles of green chemistry. Some ionic liquids, for example, 1-butyl-3-methylimidazolium chloride, are relatively effective solvents for cellulose. In classical solvents, this process occurs only under very harsh conditions. But progress does not stand still and now a new type of solvent has been proposed - deep eutectic solvents (DES). DES is an eutectic mixture consisting of a hydrogen bond donor and an acceptor. When mixed, liquid is formed with a much lower melting point than the individual components. DES is much cheaper than its predecessor and is synthesized from biodegradable components, which suggests that DES is not just an improved IL equivalent, but a new generation of solvents.

In the present work, the possibility of using DES is based on choline chloride and glutaric acid for the separation of azeotropic mixtures formed by alcohols and esters. The liquid-liquid phase equilibrium has been studied for ethanol-ethyl acetate, n-propanol – n-propyl acetate and n-butanol – n-butyl acetate mixtures with deep eutectic solvents at temperatures of 313.15 and 323.15 K. The compositions of coexisting organic and DES- phases have been determined. On the basis of experimental data on the compositions of coexisting phases, the pow coefficient of alcohol and ester, as well as the selectivity of alcohol extraction, have been calculated and analyzed.

**Acknowledgements**. This study was supported by the Russian Foundation for Basic Research (project no. 16-33-60128 mol_a_dk). The experimental work was facilitated by the equipment of Magnetic Resonance Research Centre at St. Petersburg State University.

# The method for obtaining collapsed monolayers on a target for MALDI analysis

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Immobilized metal affinity chromatography (IMAC) is of interest as a preparative method of analytical chemistry, it be a technology with a very wide range of applications, including in the case of chromatographic purification. Langmuir-Blodgett films can be sorbents for IMAC. Recently, monolayers based on iron, copper and nickel stearate have been successfully used as a sorbent by extraction with batch chromatography in spin columns to enrich the phosphopeptides from the hydrolyzate of HeLa cells [1] for extracting various pesticides and blood proteins [2, 3]. An important factor for metal-affinity sorbents is their specific surface area. To increase the specific surface area of such regular structures, a method has been proposed for transferring collapsed monolayers onto a solid substrate. However, the way including obtaining of collapsed monolayers directly on the target is more convenient

That is why we made the assumption that a monolayer can be obtained on a drop when the geometry of the drop of the subphase on a hydrophobic surface causes the formation of a monolayer, and the rate of evaporation of hexane ensures the collapsing of the monolayer at the time of production. It was proved to obtain a monolayer according to the proposed method by the LDI analysis. We used Raman spectroscopy in order to prove the formation of collapsed films.

**Acknowledgments.** The authors of the article express their gratitude to the staff of the Research Park at the SPSU for helpful assistance: resource center «Geomodel», «Centre for Molecular and Cell Technologies», «Chemical Analysis and Materials Research Centre» and «Nanophotonics Centre».

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# Comparative study of photocatalytic and bactericidal activitiesof functional coatings based on $TiO_2$ and ZnO

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Nowadays there are many new places for applications of self-cleaning materials, such as facades of buildings, anti-fog mirrors, and so on [1-2]. The production of materials with self-cleaning properties, including antibacterial action, is rapidly developing. Such materials are supposed to be used in areas from the food industry to medical and public institutions to prevent the development of pathogenic bacteria.

Earlier in our research group it was conducted the study of the photoinduced surface hydrophilicity of thin films based on *ZnO* and $TiO_2$ [3] It was found that the photoinduced hydrophilicity is decreased in following order:

$$TiO_2 > TiO_2/ZnO > ZnO/TiO_2 > ZnO.$$

In continuation of this work, the photocatalytic and photoinduced antibacterial properties of synthesized coatings based on *ZnO* and $TiO_2$ were studied and compared each other.

The coatings of individual oxides and their layer-by-layer heterostructures were synthesized by dip-coating method from sol: $TiO_2$, *ZnO*, $TiO_2/ZnO$, $ZnO/TiO_2$. The photocatalytic activity was evaluated by initial rate of photodecomposition of methylene blue (MB) in aqueous solution. Two absorption maxima of MB at 291 nm and 663 nm were used for analysis. The photoinduced antibacterial activity was tested against the *E. coli* bacteria. The reduction level value was taken for the evaluation of the inhibition degree of bacteria growth.

The obtained results and conclusions are listed below:

1. The photocatalytic activity of thin films is decreased in following order: $TiO_2 > TiO_2/ZnO > ZnO/TiO_2 > ZnO$. The photoelectrons are supposed to paly the predominant role in studied photoprocess.

2. The photoinduced antibacterial activity is decreases in opposite order as compare with previous conclusion: $ZnO \approx ZnO/TiO_2 \approx TiO_2/ZnO > TiO_2$. The *ZnO* coating exhibits the highest antibacterial activity induced by UV irradiation, while $TiO_2$ shows the least bactericidal effect in this series of coatings.

3. It is found that the ability of the photoinduced transition of the coating surface to the hydrophilic state and the photocatalytic activity of the coatings in the oxidation reaction of methylene blue change in the same order.

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# Critical phenomena in the system with n-butyl propionate synthesis reaction at 333.15 K

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In the contemporary scientific world the investigation of systems where both phase and chemical transformations take place has become demandable. Because these thermodynamic data are very useful for the process of organic synthesis and for the development of new methods that enable simultaneous separation and purification of any substance.

One of the examples of such coupled processes is critical phenomenon in propionic acid - *n*-butanol - butyl propionate - water at 333 K [1]. The object of key interest is butyl propionate due to its features as high boiling point that makes it possible to use this ester as a solvent in the chemical industry, as a flavor enhancer in the food production and etc. Therefore, the main task was to obtain critical curve for the mentioned above quaternary system (Fig. 1).

The method used for the studying of solubility is an isothermal titration or “cloud-point” technique. The solution at critical point is characterized by the constant appearing and disappearing second phase and by the blue opalescence. The fragments of the solubility curves have been applied to predict the binodal surface and it has been concluded that its shape is very different from the solubility surfaces in the systems with ethylpropionate and propylpropionate because only one binary subsystem exfoliates there [2].

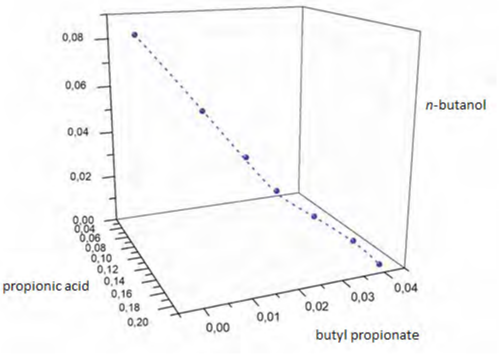

*Fig. 1. The critical curve of the propionic acid - n-butyl alcohol - n-butyl propionate – water system at 60 °C.*

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# Solubility and phase equilibrium in splitting systems with biofuel components

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Biofuels is one of the leading alternative energy sources. However, it has an inefficient production, which requires an excessive amount of raw materials, for example. Nevertheless, the organization of production can be optimized with the help of scientifically sound methods and taking into account basic thermodynamic and kinetic positions.

The composition of vegetable oils, the main component in the preparation of biodiesel, is rather complicated, so the object of the study is to provide a fundamental model system [1]. As a model, we have chosen the reaction mixture of butanol and acetic acid.

The purpose of this research is the study of solubility and liquid-liquid equilibrium (LLE) in quaternary reacting system acetic acid – n-butanol – butyl acetate – water. The research was conducted at 318,15 K and atmosphere pressure.

The experimental study of solubility was carried out by isothermal titration method. To get the solubility data the special thermostat was constructed. We used the cloud-point technique method to obtain our experimental data. The initial series of quaternary solutions were prepared with the keeping of constant ratio of acetic acid and n- butanol that is 3:1, 2:1, 1:1, 1:2, 1:3. These compositions conveniently display the form of binodal surfaces in composition tetrahedron. The experimental study of LLE was carried out by Gas chromatography method analysis for analytical determination of phase compositions.

Solubility and LLE data were obtained for the quaternary system acetic acid–n-butanol–n-butyl acetate–water at 318.15 K and atmospheric pressure. These set of new experimental data enable to present the binodal surface in composition tetrahedron. Data on solubility and phase equilibrium are well correlated and complement each other.

**Acknowledgements.** Authors acknowledge Resource Center of Saint Petersburg State University "Chemistry Educational Centre". Maria Toikka is grateful for the scholarship of President of Russian Federation (SP-2140.2016.1).

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# Laser-assisted formation of the white-light photo-emissive centers in poly(methyl methacrylate)

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Poly(methyl methacrylate)-based materials (PMMA) are increasingly being used in manufacturing of optical devices. The variety of practical applications is to a greater degree determined by different methods of laser-assisted modification of PMMA optical properties, for instance, refractive index. The currently known devices based on laser-assisted modification of PMMA are as follows: filamentary structures, 3D-microfluidic devices, gratings, lens and microlens, spots with submicrometric dimensions, colored images, three-dimensional holograms and color centers.

Laser radiant power density is one of the most important parameters in material modification below the ablation threshold. Ultrahigh irradiation energies result in appearance of damaged regions of material under examination in the previous study. Besides, it is well known that heating of the material results in erasing of color centers. The current study demonstrates white-light photo-emissive centers created in PMMA with the help of focused radiation.

Color centers were created in samples of PMMA thin films formed on oxide platforms using spin-coating. Laser modification presupposed the operation of a continuum laser (374 nm, 1 mW) and a femtosecond laser (748 and 374 nm, 200 fs, 1kHz). The irradiation was performed at two wavelengths: 748 nm (multi-photon absorption) and 374 nm (one-photon absorption via localized states).

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# SERS study and interpretation of amino substituted stilbenes behavior in metal hydrosols

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Nowadays, in the materials science there is a strong tendency to develop new optically active structures with the controllable properties. In this study, surface enhanced Raman spectroscopy (SERS) was applied to investigate an optical behavior of metal-organic nanoscale systems based on Ag nanoparticles modified by the amino derivatives of stilbene. In the previous studies, the ability of diaminostillbene (DAS) to be a molecular linker of metal nanoparticles was demonstrated by our research team. The evidence is based on the effect of «hot spots», which is expressed as abnormal Raman signal enhancement and observed when a molecule is placed in a gap between two neighboring nanoparticles. In this study, the same observations were revealed for 4-amino-4'-dimethylaminostillbene (ADMAS) in contrast to 4-aminostillbene (AS) (Fig. 1). This indicates that the tertiary amines are also able to «glue» the nanoparticles, and proves that the presence of two functional groups is crucial.

The adsorption of amino substituted stilbenes on Ag nanoparticles results in the transformation of their Raman spectra. The assumed significant shift of N-H wagging vibrational mode (~450 cm$^{-1}$) can be explained by the rearrangement of potential energy distribution in virtue of well-known donating N-TM (transition metal) interaction mechanism [1]. The quantum chemical calculations were performed to support the experimental data.

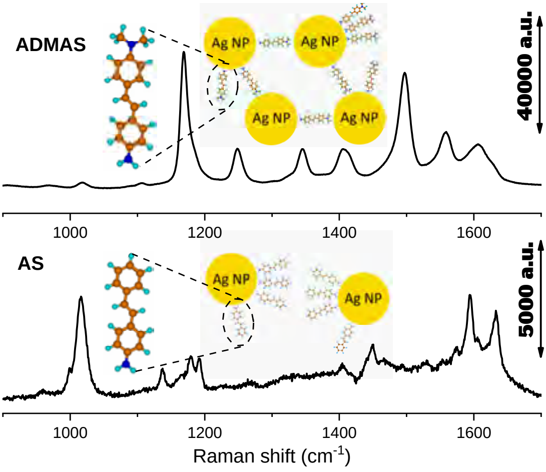

*Fig. 1. Raman spectra of ADMAS and AS in Ag hydrosol, c=10$^{-6}$ M.*

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# Cyclometalated Iridium(III) Complexes Bearing Diimine Ligands for Protein and Peptide Labeling

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Luminescent bioimaging is a rapidly developing and highly promising method for non-invasive visualization of biological systems. Nowadays iridium(III) complexes are being intensively investigated as dyes for bioimaging due to their high quantum yield, photostability, long lifetime of the excited state and relatively simple tuning of the emission parameters. This compounds conjugated with corresponding vectors can deliver a unique information on processes in living cells and tissues.

Herein we report on synthesis and characterization of iridium(III) complexes with diimine ligands and their conjugates with humane serum albumin (HSA) and peptides, which are able to pass through blood-brain barrier and selectively bind with beta amyloid peptides (Figure 1). The complexes obtained were characterized using NMR-spectroscopy, mass-spectrometry. Conjugates were investigated using mass-spectrometry and chromatography. Photophysical properties of the complexes and conjugates were extensively studied.

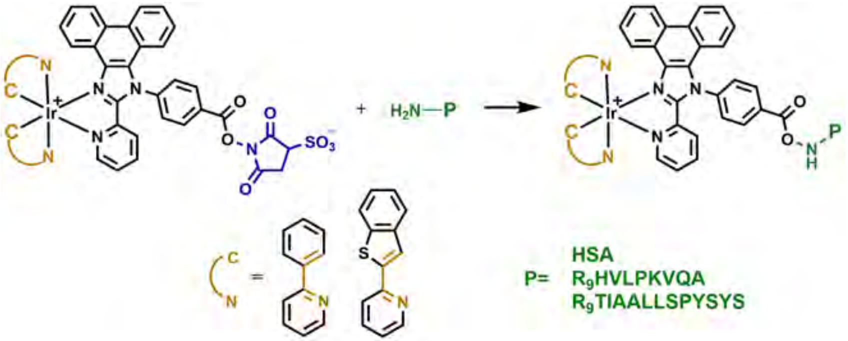

*Fig. 1. Structure of the complexes and their reaction with HSA and peptides.*

**Acknowledgements.** Financial support from Russian Foundation for Basic Research (18-33-00954) and Russian Science Foundation (16-43-03003) are gratefully acknowledge. The work was carried out using scientific equipment of St. Petersburg State University Research Park: Centers of Magnetic Resonance, Chemical Analysis and Materials Research; and the X-ray Diffraction Centre.

# Improvement of the deoxyribozyme 10-23 cleavage efficiency

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Deoxyribozymes 10-23 with RNA-cleaving activity was discovered in 1994 [1]. There were many trials about the implementation of these molecules, such as highly specific silencing of genes, treatment of viral diseases and cancer. However, this kind of molecules was not found any clinical applications because the RNA-cleavage efficiency of DNAzymes 10-23 is very low under physiological conditions. A high therapeutic concentration of deoxyribozymes leads to non-specific activity that is dangerous for their application as therapeutic drugs [2, 3].

In our work, we are trying to improve the RNA-cleaving ability of DNAzyme 10-23. The reaction has three steps: (i) generation of the complex between RNA and deoxyribozyme; (ii) cleavage reaction; (iii) dissociation of deoxyribozyme from the cleaved product.

We suppose the complex between deoxyribozyme and RNA-substrate is not stable under physiological conditions (2 mM $MgCl_2$). Moreover, we think, the secondary structure of RNA-substrate makes the energetic barrier for the cleavage. Therefore, we add two deoxyribozymes (DZ1 and DZ2) in reaction mixture to increase the probability and the efficiency of the cleavage using two sites of restriction. Then, we linked two DNAzymes 10-23 in one construct via the polyethylene glycol (PEG) (DZ1pegDZ2) and the dsDNA platform (NanoDeflu). We assume, such designs performs the cooperative effect from two deoxyribozymes and increase the stability of RNA-DNAzyme complex and unwinding of RNA-secondary structure.

As a target in our investigation, we use conservative part of Influenza A viral RNA encoding PB1-subunit of viral RNA-polymerase playing a crucial role for translation and replication of viral RNA within the cell.

Obtained data suggested the implemented designs of DNA-nanoconstructs has about 2 times greater cleavage efficiency than the single deoxyribozymes 10-23 with the same sequences. In such circumstances, we will continue our work with the different target RNA motifs in order to prove the results and optimize cleaving properties of this type of DNAzymes.

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# Ion-selective adhesive tape for potentiometric measurements of potassium and sodium ions in biofluids

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Wearable sensor systems that enable in situ monitoring of biologically significant analytes in real time have been expected as promising devices for medical purposes.

Specifically, electrochemical sensors can be utilized to detect a variety of biological markers in bodily fluids [1].

Perspiration from the human body, for example, contains biomarkers such as sodium ions, potassium ions, glucose and lactate. Physiological information obtained from sweat analysis, can be used for diagnose diseases, drug abuse detection, and athletic performance optimization [2].

Sodium and potassium ions are usually measured using a potentiometric measurement method with ion-sensitive membranes.

This research focuses on the development of simple and cost effective approaches for making electrochemical sensors with a great sensitivity and selectivity for potentiometric measurements of potassium and sodium ions. Owing to their unique properties such as light weight, low cost, high flexibility, and excellent stretchability, flexible carbon conductive adhesive tape could serve as an ideal platform for personalized wearable devices.

The sensor platform consists of adhesive tape-based that combine an ion-selective electrode with a conventional ion-selective membrane (ISM) immobilized within a permeable film of the polyelectrolyte. The required selectivity for the target analyte is achieved by using a suitable ionophore.

$K+/Na+$ sensors exhibit a relative high sensitivity (a slope close to the theoretical value), and efficiency in ranges concentration that are clinically useful (3 – 20 mM /10-160 mM).

Ion-sensing electrochemical adhesive tape-based analytical devices provide a simple, portable, low-cost, and disposable tool for measuring the concentration electrolytes in human sweat.

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# A novel technique based on microextraction in deep eutectic solvents for HPLC-FLD determination of fluoroquinolones in meat samples

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Antibiotics are used not only to treat food animals but also to prevent them from developing diseases and to promote their growth. Abuse in food animals has important consequences for public health, as it promotes the development of antibiotic-resistant bacteria and resistance genes that can be passed on to people [1]. Thus, the monitoring of antibiotics presence in food products is an important challenge of public health.

In the current study, a novel microextraction technique based on using deep eutectic solvents (DES) as effective extractant for fluoroquinolones has been developed. The new approach involves in situ DES generation from quaternary ammonium salt and alcohol under heating and mixing in extraction vessel with treated meat sample with following extraction of target analytes into the DES. After centrifugation the top organic phase was analyzed by HPLC-FLD, and concentrations of fluoroquinolones were determined according to the calibration curve. This method can be characterized as sensitive, simple, low cost, and environmentally friendly due to avoiding the use of toxic solvents for the extraction step. The proposed method was successfully applied for the HPLC-FLD determination of two antibiotics (ofloxacin and fleroxacin) in beef and chicken meat samples, and analytical results agreed well with the results obtained with reference technique.

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# Aggregation behavior of surface active amino acid ionic liquids (1-alkyl-3-methylimidazolium lysinates) in water

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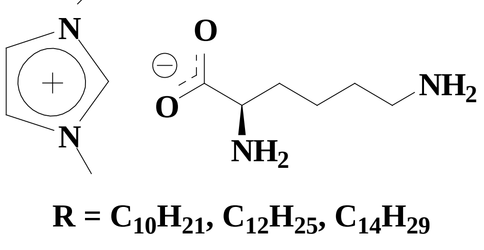
Amino acid ionic liquids (AAILs) with the long alkyl tails (n > 8) are considered as new type of cationic surfactants, which have a tendency to self-organization and show a high ionic conductivity. Because of strong hydrogen bonding these «green» ILs have shown excellent ability to dissolve different substances such as biomaterials in separation processes.

In this work, a number of AAILs [C$_n$mim][Lys] (n = 10, 12, 14) based on 1-alkyl-3-methylimidazolium as the cation and L-lysine as the anion were synthesized and characterized by NMR spectroscopy (Fig. 1). The data on specific conductivity and on surface tension were obtained for the aqueous solutions of AAILs of different concentrations at 298.15 K and atmosphere pressure. From these data, some characteristics of the micellization process, namely critical micelle concentration (cmc), degree of counterion binding ($\beta$), and standard Gibbs energy of micellization ($\Delta G^0_m$) were determined. Besides, the molar partition coefficients between micelles of [C$_8$mim][AA] (AA = Lys, L-Leucine, Cl) and the aqueous surrounding ($k_{mic}$) for L-tryptophan as model solute were estimated by means of micellar-enhanced ultrafiltration as well as of NMR diffusometry. The data obtained by different methods are in a good agreement. The obtained results clearly show that the general features of micellar aggregation of relatively long-chain alkylmethylimidazolium ILs with amino acidic anions in aqueous solutions are similar to those for conventional ionic surfactants.



$R = C_{10}H_{21}, C_{12}H_{25}, C_{14}H_{29}$

*Fig. 1. Structure of AAILs [C$_n$mim][Lys], where n = 10, 12, 14.*

**Acknowledgements.** The work was financially supported by the Russian Science Foundation (grant 16-13-10042). The NMR measurements were carried out at the Center for Magnetic Resonance, St. Petersburg State University.

# Self-assembled polypeptide particles as dexamethasone delivery systems

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Self-assembled systems from biodegradable amphiphilic polymers have attracted much attention especially in biomedical fields. In our case, synthetic random polypeptides were chosen as the polymer systems for the development of dexamethasone delivery system. With this aim, amphiphilic copolymers consisting of hydrophobic L/DL-phenylalanine and hydrophilic L-lysine and differed with monomer ratio were synthesized using ring opening polymerization of corresponding N-carboxyanhydrides. The synthesized copolymers were characterized with enough narrow molecular weight distribution ($M_w/M_n \leq 1.4$). Copolymer composition was determined using quantitative HPLC analysis after acidic hydrolysis of polypeptides to free amino acids.

The results obtained by transmission electron microscopy clearly showed that copolymers poly(*L*-lysine-co-*L/DL*-phenylalanine) were really capable to self-assembling in aqueous solutions forming the nanospheres. In the series of copolymers P(*L*-Lys-*co*-*L/DL*-Phe) the hydrodynamic diameters of the particles in water were from 90 to 300 nm. PDI values for all samples were lower than 0.3. The biodegradation of P(*L*-Lys-*co*-*L/DL*-Phe) nanoparticles was evaluated using in vitro degradation in a model systems, containing enzymes (papain, proteinase K). It was proved that polymer particles formed from *D,L*-phenylalanine as hydrophobic units were more stable to degradation than L-containing polymers.

Encapsulation of model hydrophobic compound, namely, dexamethasone, into polymer particles was carried out and dependence of encapsulation efficiency on polymer composition was studied. Dexamethasone-loaded nanoparticles released the drug in 30 days. An average release within the first week was found to be 6.0 ± 2.5%. The study of the cytotoxicity of the nanoparticles developed was carried out using CTB-test and human embryonic kidney cells (HEK-293). The nanoparticles developed were found to be slightly toxic ($EC_{50}$ = 50 μL/mL). The covering of nanoparticles with heparin improved the biocompatibility of the polymer particles with cells ($EC_{50}$ >420 μL/mL).

**Acknowledgements.** The reported study was funded by RFBR (the research project № 18-33-01018). Additionally, the authors are grateful to Chemical Analysis and Materials Research Centre of St. Petersburg State University for HPLC analysis.

# Development and investigation new pervaporation membranes based on PVA prepared with surface and bulk modification

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Currently membrane methods are alternative processes to traditional separation methods due to good characteristics. Pervaporation is a well-known membrane separation process, which is attractive and widely used in different industrial fields as an alternative process to distillation or liquid-liquid extraction. The potential of this process is especially suitable for the dehydration of different mixtures. The rapid development of membrane processes, in particular pervaporation, requires the essential improvement of the transport properties of polymer membranes that can be achieved by one of the promising and effective methods - the modification of the polymer matrix by inorganic filler to develop the mixed-matrix membranes (MMMs). MMMs combine advantages of both an inorganic and organic components and they offer the possibility to overcome the trade-off between the permeability and selectivity of the polymeric membranes. Among inorganic particles, fullerene takes an important place, since this nanoparticle retains its unique π-electronic structure inside of the polymer matrix.

In the present work the novel supported membranes based on polyvinyl alcohol were prepared by bulk and surface modification. Bulk modification was carried out by introducing the polyelectrolyte (poly (allylamine hydrochloride)) and water-soluble fullerene derivative (fullerenol). Surface modification was carried out by layer by layer deposition with application of two polyelectrolytes (polyallylamine hydrochloride and sodium polystyrene sulfonate). Physico-chemical properties of the developed membranes were studied by scanning electron microscopy and contact angle measurements. Transport properties of the membranes were investigated by pervaporation during separation of water-organic binary mixtures: isopropyl alcohol – water and tetrahydrofuran – water.

**Acknowledgements.** This work was supported by Russian Science Foundation [grant No. 17-73-20060]. The experimental work was facilitated by equipment from Resource Centers: for Nano technology, X-ray Diffraction Methods, Thermal Analysis and Calorimetry, Chemical Analysis and Materials Research Centre and GEOMODEL at St. Petersburg State University.

# Determination of key factors controlling stability of liposome-microgel complexes

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Liposome-microgel complexes can be potentially used as a drug delivery system. In comparison to free liposomes, complexes may provide certain advantages such as bigger amount of a therapeutic agent that can be delivered per one carrier and ability to encapsulate several drugs in different compartments preventing them from interaction with each other.

In this work we prepare complexes from negatively charged liposomes and positively charged microgels. Since this structures are electrostatic in their nature, a reasonable question arises: are they stable at physiologically relevant ionic strengths (150-200 mM)?

To address this issue a) aggregation profile was followed with dynamic light scattering to determine the range of liposome-to-microgel ratios where interaction can be observed; b) aggregation profiles were then followed at different ionic strengths to establish whether interaction of charged surfaces occurs; c) once ionic strengths at which interaction stops were determined, release kinetics was studied with use of fluorimety to check the effect of salt on leakage rate.

The main factors determining stability of complexes in water-salt media were determined to be pH and surface charge density.

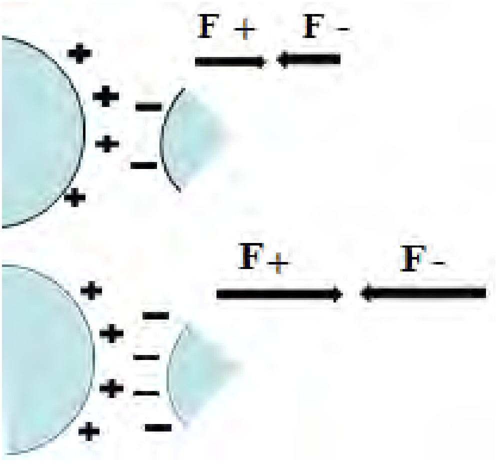

*Fig. 1. Simple model of interaction of charged surfaces.*

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# A prospective study on Kapton polymer membranes for pervaporation

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Pervaporation, combining permeation and evaporation processes, has been regarded as an effective membrane separation method. Azeotropic liquid mixtures and high-boiling liquids can be separated without high-energy consumption and usage of extra compounds.

Polymer structure widely defines the properties of the membranes that are used for separating organic solutions. The aim of this work is a fabrication of novel asymmetric membrane and investigation of its transport properties in the pervaporation processes. Asymmetric membranes have many advantages in comparison with homogeneous membranes determined by the features of their structure. The asymmetric membrane has a thin selective layer and a porous substrate, which makes it possible to combine the high selectivity provided by a dense layer and the high flux that occurs in the case of thin membranes with increased mechanical strength.

In this work, the polymer (4-oxidodiphenylene) pyromellitimide (Kapton) was first tested in a pervaporation process. This polymer was used to fabricate homogeneous and asymmetric membranes. Currently, Kapton is widely used in industry since it has low cost and operation stability.

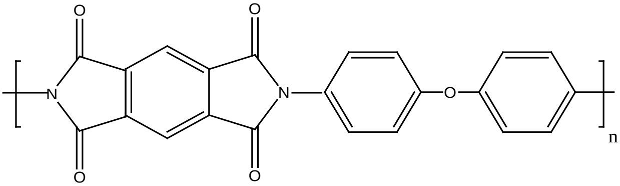

*Fig. 1. Kapton PMDA-ODA.*

Novel polymer membranes were used to separate the mixture methyl-t-butyl ether (MTBE) - methanol in the process of pervaporation. In the course of the work mass transfer through the membrane was investigated by sorption experiments which showed that the Kapton membrane mainly sorbes methanol and is inert to the ether.

Asymmetric membrane demonstrated flux that was nearly 15 times higher than for homogeneous membrane, meanwhile, selectivity remained unchanged.

**Acknowledgments.** Equipment of Resource Centers of St. Petersburg State University, namely, “Chemical Analysis and Materials Research Centre”, Interdisciplinary Resource Center “Nanotechnologies” and “Thermogravimetric and calorimetric methods of investigation” were used for membrane investigation.

# Synthesis and reduction of the adducts of *N*-aryl itaconimides with nitrones

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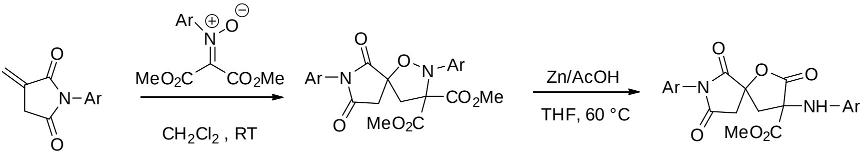
The isoxazolidine ring represents one of the privileged structures in medicinal chemistry due to its potential biological activity. Substituted isoxazolidines are able to exhibit anti-inflammatory, antiviral and antimicrobial activity [1]. Imides of itaconic acid are interesting dipolarophiles due to the presence of an activated exocyclic double bond. Therefore 1,3-dipolar cycloaddition reactions of itaconimides with nitrones offer a simple route to rare classes of heterospiro compounds which are hard-accessible otherwise. It is known that isoxazolidines can be easily opened with a cleavage of  N-O bond when acted upon by various reagents to form 1,3-amino alcohols, the subsequent intramolecular cyclization of which can lead to different classes of organic compounds. That has been studied by our research group[2].

The aim of this work is to investigate regioselectivity of 1,3-dipolar cycloaddition of *N*-aryl itaconimides with *N*-aryl-*C,C*-bis(methoxycarbonyl)nitrones and to study subsequent transformation of formed isoxazolidines.



It was found that the cycloaddition reaction proceeds regioselectively to form isoxazolidines as a single 5-spiro regioisomer. Also it was found that the reduction of N-O bond gave the 1,3-amino alcohol as the intermediate which then in the presence of an ester function in the C3 position underwent a spontaneous cyclization yielding the α-amino lactone.

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# Dilatational rheological properties of $C_{60}$-arginine and $C_{60}$-L-lysine adsorption layers

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The adsorption layers of two derivatives of fullerene $C_{60}$ with lysine and arginine (Fig. 1) at the media/air interface were investigated by surface tensiometry, dilational surface rheology, capillary wave method and the Brewster angle microscopy. The conjugates of $C_{60}$ with lysine and arginine ($C_{60}$-Lys and $C_{60}$-Arg) unlike many other derivatives of fullerenes are soluble in water because of the presence of amphiphilic amino acid residues. This gives a possibility to form self-organized films of fullerene derivatives at the water surface without application of the complicated procedure of the layer spreading. The adsorption is irreversible, and the derivatives under investigation can form a dynamic network at the interface with almost zero surface pressure and high dynamic surface elasticity up to about 100 mN /m. It is shown that the adsorption layers of $C_{60}$-Lys and $C_{60}$-Arg are characterized by strongly different rheological properties and different morphologies. The layers of $C_{60}$-Arg are fragile while those of $C_{60}$-Lys are liquidlike. The distinctions in the properties are mainly caused by different amounts of amino acid residues in fullerene $C_{60}$ derivatives.

**Acknowledgements.** The work was financially supported by the Russian Foundation of Basic Research and Ministry of Science and Technology of Taiwan (joint project № 16-53-52034_MHT_a and a project № 16-08-01206).

# Processes in reacting mixtures containing methyl oleate and ethyl oleate

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Coupled processes are significant not only from the fundamental aspect of the development of science, but also have a direct application value for energy - and resource - saving environmentally friendly technologies. The importance for chemical technology is determined by the application in many industries, for example in the technology of basic organic synthesis and separation of substances, reactive distillation. Inclusion in the technological schemes of coupled processes can significantly reduce energy and resource costs per unit of the target product and increase the environmental friendliness of the process as a whole [1-3]. Phase and membrane processes are widely used for compound purification, wastewater treatment, concentration and fractionation of industrial liquid and gas mixtures. Pervaporation is a membrane process for the separation of liquid mixtures that allows the separation of mixtures containing near-boiling components or azeotropic mixtures. Modern problems of chemical technology are determined by the relevance and need for the development of combined phase and pervaporation processes.

This paper presents new experimental data on the separation of reaction mixtures containing methyl oleate and ethyl oleate. Data on the transport and physical-chemical properties of membranes (including hybrid process) are presented.

**Acknowledgements.** Authors acknowledge Resource Center of Saint Petersburg State University "Chemistry Educational Centre". Maria Toikka is grateful for the scholarship of President of Russian Federation (SP-2140.2016.1).

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# Production of biodiesel based on coupled processes

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The growing interest of coupled processes in multicomponent systems in the scientific community, namely the annual increase in the number of publications (in journals Chem. Eng. Sci., Chem. Eng. Data, Fuel [1], Fluid Phase Equilibria and others) and researchers groups in this field, confirms the significance of these results not only from a fundamental point of view, but also from a multiple applied orientation. One of these areas of energy-saving technologies and to develop them requires knowledge of thermodynamic and physical-chemical parameters in different systems, methods for determining these values. Energy-saving technologies include such areas as biodiesel and the development of schemes to improve the energy efficiency of equipment. In this paper, thermodynamic features of systems directly related to the latter directions are considered. Investigation of phase and chemical equilibrium is technologically important in the synthesis schemes separation of the reaction mixtures and the synthesis reaction system includes esters are basis for obtaining biodiesel.

This work report data on the phase and chemical equilibrium (40, 50ºC) for a systems contain ethyl acetate, methyl oleate and ethyl oleate. Here we report the results of study of chemical equilibrium in this system at several temperatures (40 and 50°C). The experimental data on chemical equilibrium was obtained by two different methods: gas chromatography and nuclear magnetic resonance spectroscopy.

**Acknowledgements.** Authors acknowledge Resource Center of Saint Petersburg State University "Magnetic Resonance Research Centre". Maria Toikka is grateful for the scholarship of President of Russian Federation (SP-2140.2016.1). Alexandra Golikova acknowledges for the Scholarships of President of Russian Federation (SP-2680.2018.1).

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# Modeling possible transformations of the (benzene) ruthenium dichloride dimer in water-THF-acetic acid solutions under CO atmosphere

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Ruthenium complexes are efficient precatalysts for unusual reductive amidation and amination reactions that proceed under CO atmosphere [1]. Carbon monoxide is known to act as a reductant in these processes. However, the structure of the catalytic centers, as well as the reaction mechanism remains elusive. We used quantum chemical methods to investigate possible transformations of (benzene)ruthenium dichloride precatalyst under CO atmosphere in the water-THF mixed solvent.

The Konh-Sham DFT calculations with the hybrid PBE0 functional and D3-dispersion corrections were performed. We used the Gaussian 6-311G(d,p) basis set for all atoms except Ru. In the latter case, the SDD basis set was used. Unconstrained geometry optimizations and vibrational frequency analysis were performed with Gaussian 16 program package. The bulk solvent effects were taken into account with polarizable continuum model (PCM). On the basis of the calculation of different possible transformations of the catalyst [2] and estimation of the corresponding thermodynamic parameters, we propose the octahedral ruthenium complex with CO and water ligands (Fig.1) as the most thermodynamically stable form under the given conditions.

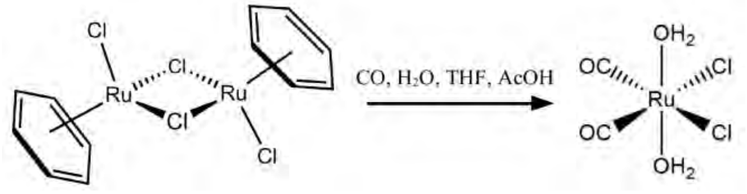

*Fig. 1. The most thermodynamically favorable transformation of the (benzene) ruthenium dichloride dimer in water-THF-acetic acid solutions under CO atmosphere according to the PBE-D3(BJ)/6-311G(d,p)&SDD calculations.*

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# The effect of the synthesis parameters on the properties of β-$NaYF_4$:Yb,Tm up-converting nanoparticles

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Fluorescent nanoparticles β-$NaYF_4$:$Yb^{3+}$,$Tm^{3+}$ due to their optical properties have a great potential for applications in bio-imaging as fluorescent labels and imaging probes. We have studied the influence of the synthesis parameters on the luminescent properties of $NaYF_4$ nanoparticles co-doped with $Yb^{3+}$ and $Tm^{3+}$. The effect of the purity of the reagents, the concentration of the stabilizing ligand (oleic acid), the effect of water in the reaction mixture on the fluorescence of β-$NaYF_4$:$Yb^{3+}$,$Tm^{3+}$ nanoparticles have been demonstrated in our work.

The nanoparticles with that were synthesized by solvothermal method. The morphology of the obtained nanoparticles was studied by transmission electron microscopy. They have spherical structures and size of around 20 nm. The up-conversion fluorescence of β-$NaYF_4$:$Yb^{3+}$, $Tm^{3+}$ nanoparticles dispersed in ethanol was measured at 980 nm excitation wavelength. The sample exhibited blue luminescence, which originated from the $^1D_2 \rightarrow {}^3H_6$, $^1I_6 \rightarrow {}^3F_4$ transitions of $Tm^{3+}$.

**Acknowledgements.** The measurements where performed in the "Centre for Optical and Laser materials research", "Interdisciplinary Center for Nanotechnology", "Centre for Molecular and Cell Technologies" and "Cryogenic department" of Research Park of Saint-Petersburg State University.

# Deep eutectic solvents as a new kind of green dispersive solvents for dispersive liquid-liquid microextraction. Determination of bisphenol-a in soft drinks

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Since DLLME was became, this method has quickly gained popularity because of its simplicity, low cost and high availability. The extraction procedure includes a rapid injection of the disperser solvent containing extractant. The fast injection produces a cloudy solution of small droplets of extraction solvent (immiscible with water) in the homogeneous water-disperser solution. In the DLLME, large surface contact between fine organic droplets and sample speeds up the processes regarding mass-transfer of analytes from aqueous phase to organic phase which greatly enhances extraction efficiency. The main disadvantage of the DLLME is the need of using an additional dispersive organic solvent that can increase solubility of the hydrophobic analytes in an aqueous phase reducing the extraction efficiency

One environmentally friendly alternative to conventional dispersants is using of deep eutectic solvent (DES). DESs have attracted great interest in many fields as a new generation of green and sustainable solvents. They are usually prepared by simply mixing two components, a hydrogen-bond donor (HBD) and a hydrogen-bond acceptor (HBA) with forming a liquid with melting point lower than that of each component. DESs, as a subclass of ionic liquids, show comparable characteristics; they are cheaper and easy to be produced due to lower cost of the raw materials, less toxic and often biodegradable.

In this study, dispersive liquid–liquid microextraction using of deep eutectic solvent (DES) as a “green” dispersant resulting analyte extraction was established for the first time. The suggested approach was applied for development of high-performance liquid chromatography with fluorescence detection (HPLC-FLD) method for the bisphenol-a determination in beverages samples (still water, sparkling water and orange juice.

**Acknowledgements.** Andrey Shishov gratefully acknowledges financial support for research from Russian Scientific Foundation (project no. 18-73-00111). HPLC-UV assay was performed at the Chemistry Educational Centre of Research Park of St. Petersburg State University.

# Atomic spectral determination of essential and toxic elements in tea leaves and tea

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Tea is one of the most popular non-alcohol beverages. It contains many chemical compounds with taken into the human organism. That is why determination of substances, including essential and toxic metals, in tea leaves and beverages is an important task of food chemistry. The aim of this work is comparative determination of trace elements content of different types of tea sample. Many researches work with black tea as a sample studied. However, it's known, that green tea contains more bioactive substances such as caffeine, tannins, aromatic acids. In our work we also decided to analyse green tea samples, particularly tea of different flavours from the one brand line, widely represented in the Russian market.

To determine elemental concentrations we use atomic emission spectrometry with inductively coupled plasma. In case of tea leaves analysis preliminary microwave mineralization samples was made as digestive procedure. Tea beverages were analysed after dilution.

Data on concentration of Al, B, Ba, Ca, Cu, Fe, K, Mg, Mn, Na, Ni, Sr, Zn in several tea samples are presented. These data are in good agreement with the literature ones. Cd and Pb was not detected in studied samples, but LODs of these elements are smaller than maximum permissible concentrations for tea. Results of comparative analysis of elements content of different types of tea samples are presented, as well as of tea leaves and respective beverages.

Scientific research were performed at the Research Park of St. Petersburg State University «Educational Resourse Center of Chemistry» and «Center for Chemical Analysis and Materials Research».

# A study of protonated forms of layered perovskite-like niobate $KCa_2Nb_3O_{10}$ and their reactivity with methanol

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Layered perovskite-like niobates $AB_2Nb_3O_{10}$ (A = alkali cation, B = Ca, Sr, Ba, Pb), relating to Dion-Jacobson phases, are solid crystalline compounds, in which blocks with perovskite structure $[B_2Nb_3O_{10}]^-$ alternate with interlayer spaces, containing alkali cations $A^+$. [1] These compounds are well known as basis for creating catalysts, photocatalysts, materials for electronics, etc. One of their key features is the ability to undergo ion exchange. In particular, in aqueous solutions of acids replacement of alkali cations $A^+$ by protons takes place.[2] Practically, protonated forms obtained in this way are solid acids and, consequently, are able to react with some organic substances (amines, alcohols, etc.), forming organic-inorganic hybrids.

The present work is devoted to synthesis and characterization of different protonated forms of the layered perovskite-like niobate $KCa_2Nb_3O_{10}$ containing different amounts of intercalated water, as well as to investigation of their reactivity with methanol. Possibility of the methanolic hybrids synthesis is studied under various conditions using the solvothermal technique. Role of interlayer water on the ability to form methanol derivatives with $HCa_2Nb_3O_{10}$ was investigated. Suitable ways of producing single-phase methanolic derivatives are established. Characterization of the products is performed with an emphasis on their structure, composition and morphology.

**Acknowledgements.** This research was supported by RFBR (grants № 16-33-60082, № 16-33-60044 and № 18-03-00915). Authors also are grateful to Saint Petersburg State University Research Park: Center for X-ray Diffraction Studies, Center for Chemical Analysis and Materials Research, Center for Thermal Analysis and Calorimetry, Interdisciplinary Center for Nanotechnology.

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# Synthesis and characterization of $GdFe_{1-x}Co_xO_3$ nanoparticles for catalytic application

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Perovskite-type oxides have been used in a wide range of applications as catalysts owing to their high catalytic activity, thermal stability and relatively low cost. Especially rare-earth cobaltites were found to be catalysts for total oxidation of CO and hydrocarbons and for simultaneous reduction of $NO_x$ [1].

New nanopowders of $GdFe_{1-x}Co_xO_3$ (x = 0; 0.2; 0.5; 0.8; 1) were synthesized by the modified sol-gel method elaborated previously for ferrites [2], by dissolving of $Co(NO_3)_2 \cdot 5H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$ and $Gd(NO_3)_3 \cdot 5H_2O$ in distilled water along with citric acid and calcination at 800°C at air as last stage. Phase analysis, lattice parameters and crystallites sizes determination were performed by X-ray powder diffraction using a Rigaku MiniFlex II diffractometer with CuKα radiation. The morphology of samples was studied by SEM using Carl Zeiss EVO 40EP and Zeiss Supra 40VP instruments. BET surface area was determined from $N_2$ adsorption isotherm with a Nova 4200e Quantachrome system. The XRD pattern of of $GdFe_{1-x}Co_xO_3$ (x = 0; 0.2; 0.5; 0.8; 1) shown in Fig. 1a can be indexed in the orthorhombic structure with Pbnm space group without any traces of secondary phases. Fig.1b shows SEM image of $GdCoO_3$ nanoparticles, the particle size order 100 – 200 nm, the surface area – 6,27 m²/g. It will be present examples of catalytic activity of synthesized samples in some practically important processes.

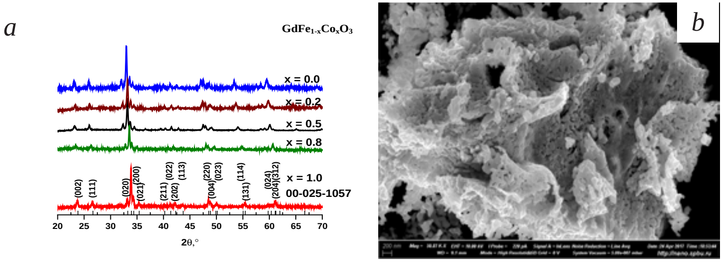

*Fig. 1. a - XRD pattern; b- SEM of $GdCoO_3$ nanoparticles.*

**Acknowledgements.** This work was supported by the Russian Foundation for Basic Research (№ 18-33-01209). Scientific researches were performed at the Center for X-ray Diffraction Methods and Interdisciplinary Center for Nanotechnology of Research Park of St. Petersburg State University.

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# Preparation of liposome-encapsulated magnetite for construction of thermo- and magnetosensitive liposome-microgel complexes

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Recent reviews on drug delivery systems outline that further development of such systems should result in embedding stimuli-sensitivity and ability to carry several therapeutic agents simultaneously. These requirements can be satisfied with the system composed of liposomes bound to a thermosensitive microgel. Microgels of certain composition may undergo significant decrease in size (collapse) upon heating. As a result, instability of microgel-bound liposomes may be induced which may lead to release of encapsulated drug. This system can be upgraded by adsorption of one more type of liposomes, namely, liposomes loaded with magnetic nanoparticles. Such modification of liposome-microgel complexes may allow control of delivery and release with magnetic field.

We have experimentally demonstrated that anionic liposomes made of egg lecithin and phosphatidylserine can be adsorbed on the surface of cationic microgel synthesized from 3-(*N,N*-dimethylamino)propylmethacrylamide, *N*-isopropylacrylamide and *N,N*-methylenebisacrylamide. Liposomes stay intact upon adsorption and the release of doxorubicin, antitumor antibiotic, preliminary encapsulated into liposomes, can be induced by heating the system up to the temperature of microgel collapse.

For the synthesis of magnetic nanoparticles a well described citrate method was adopted from the literature [1]. This method employs co-precipitation of iron salts with consequent stabilization of particles with citrate molecules. The excess of citric acid is then eliminated with dialysis. Though particles initially form agglomerates, deprotonation of surface-adsorbed citrate molecules at higher pH values leads to increase in absolute surface charge density and formation of colloidally stable particles [2]. First attempts at synthesis revealed that formation of magnetite nanoparticles of 20-50 nm stable in solution with pH = 7.2 is a result of intricate balance between particle concentration and time of dialysis. As the next step, magnetite nanoparticles were encapsulated into liposomes. Magnetite-containing liposomes were adsorbed onto the surface of microgel.

The reported study was funded by RFBR according to the research project № 18-33-01190.

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# Magnetite nanoparticles as enzymatic mimetics in activating of anticancer prodrugs

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Nowadays nanomaterial-based enzyme mimetics have attracted enormous attention. The reason lies in the combination of high catalytic activity and a number of advantages over natural enzymes: high resistance to harsh conditions and storage, as well as ease of synthesis with the possibility of scaling. However, medical applications of mimics are largely limited by biosensors, immunoassay, and diagnostics, while areas such as the treatment of diseases, such as cancer, remain unexplored or poorly understood [1].

We propose a fundamentally new approach−to use magnetite nanoparticles as a peroxidase mimetic in activating antitumor prodrug agents, such as indole-3-acetic acid [2]. The existing method has several disadvantages, including the instability of the enzyme, which activates the oxidation of the prodrug. At the same time, the magnetite obtained in our laboratory has a number of advantages, among them biocompatibility [3], high stability, high catalytic activity, the possibility of targeted delivery, since the particles are paramagnetic. Another feature of the study is the use of magnetite hydrosol in the synthesis of which stabilizing additives are not used.

In present study peroxidase-like activity of magnetite was investigated by typical colorimetric reaction involving hydrogen peroxide ($H_2O_2$) and chromogenic reagent - ABTS. The formation of reactive oxygen species was determined using the standard agent for fluorescence spectroscopy – DCFDA.

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# The thermodynamic study of chemical equilibrium in ternary system

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In the framework of this work the condition of chemical equilibrium was combined with the stability condition. It's necessary for finding a critical point that makes it possible to research critical states, phase and chemical equilibrium together.

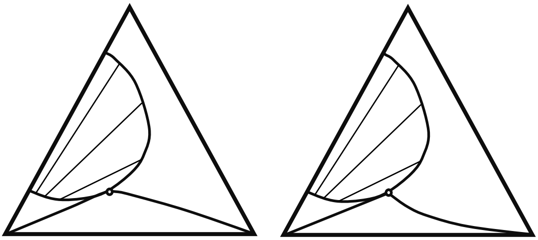
a b

*Fig. 1. The relative position of the binodal and the chemical equilibrium curve a - single degeneracy of the determinant, b - double degeneracy of the determinant.*

In binary systems the combination of the determinant $\mu_{11}\mu_{22} - \mu_{12}^2 = 0$ and the chemical equilibrium condition $n_1\mu_1 + n_2\mu_2 = 0$ gives the following interrelation $\mu_{11} = \partial\mu_1/\partial n_1 = 0$. It's equivalent to the independence of the chemical potential from the amount of substance. It was decided to consider the ternary system and combine the same conditions. The graphic representation of the chemical equilibrium in the three-component system is the Gibbs-Rosebom triangle. When the chemical equilibrium curve and the binodal are crossed, they can have one common critical point. In the ternary system the stability condition is the determinant corresponding to the binodal:

$$\begin{vmatrix} \mu_{11} & \mu_{21} & \mu_{31} \\ \mu_{12} & \mu_{22} & \mu_{32} \\ \mu_{13} & \mu_{23} & \mu_{33} \end{vmatrix} = 0, \text{ where } \mu_{ij} = \partial\mu_i/\partial n_j.$$

At the same time, the condition $\sum n_i\mu_i = 0$ corresponding to the chemical equilibrium curve will also satisfy to the critical point. So that their combination opens the possibility of theoretical research of the behavior in the critical point and its proximity, particularly of the chemical equilibrium curve.

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# B.Geo- and Astrophysics

# Investigating the role of Lunar remanent mini-magnetospheres for deflection of the solar wind

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Moon does not have global dipole magnetic field since it does not possess the internal dynamo driven by convective motions within the core. However, the Lunar crust contains areas of large remanent magnetization, the so-called Lunar Magnetic Anomalies (LMAs). Some of them are strong enough to stand-off the solar wind dynamic pressure and create a minimagnetosphere, which shoots and deflects impinging ions back in the solar wind. This work investigates the correlation between two datasets which are used to study LMAs. The first dataset is based on a global spherical model of Lunar magnetic field developed by [Tsunakawa, 2015], and the second dataset measures reflection of solar wind ions [Lue, 2011]. The study shows that the large |**B**| regions have considerably more pronounced flux of deflected ions. The correlation between the **B** field model and reflection coefficient peaks at ~25-30 km above the Lunar surface, which likely corresponds to vertical extent of the formed mini-magnetospheres. Reflected ion flux contains two extremely different components (which are resolved by reflection coefficient), namely 1) uniform anti-streaming scattered component with «1% reflection coefficient nearly independent of magnetic field (dominates for surface B<5 nT) and 2) anomalous component which is pronounced for surface B>40 nT and which increases with magnetic field. In the middle B field range (0… 100 nT) the reflection coefficient grows as a shifted hyperbolic tangent function from a uniform value of ~0.03-0.07% (near 0 magnetic fields) up to ~10% (anomalous reflection component typical for large >100 nT surface magnetic fields).

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# The forward modelling and measuring system selection in the self-potential method for mineral exploration

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The self-potential method is geophysical method with natural source of the electric field. It involves measurements of electric potential on the surface in order to find underground currents. By distribution of obtained data it becomes possible to choose which kind of source is buried and explore some special characteristics of that source. The method is traditionally popular among geophysicists since it was first applied by Fox (1830) [2]. It finds use in mapping and geoprospection of conductive ores.

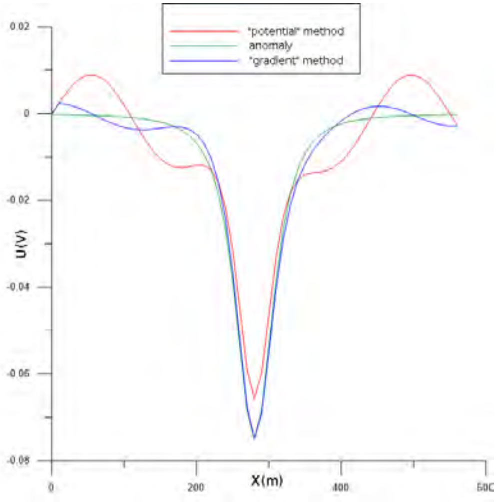

*Fig. 1. Comparing data observed by potential measurement system and gradient-based one.*

Nowadays geophysicists still have no strict position on measuring system. The aim of the study was to make reasonable selection (Fig. 1) between gradient-based approach and "potential" system – two main systems. Besides, in the work convenient software for forward modeling was implemented based on works of Semenov [3] and Akgün [1]. This work would be interesting for practicing geologists.

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# Study of the stability of the preliminary orbit of mu Cet

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With the observational data obtained at the SAO RAS 6-m telescope, an interferometric orbit of system containing a nearby A-giant mu Cet was constructed for the first time. The orbit has a preliminary status due to the lack of measurements of the positional parameters for the interval of epochs of several years. This required a study of the sustainability of the obtained solution. For this, a grid with six orbital parameters was selected in the neighborhood of the existing solution. At each point using the Levenberg–Marquardt algorithm the nearest local minimum was found. To evaluate the solutions, the chi-square test was used. We discuss the estimates of the sum of the masses of the components of the system mu Cet, which can be obtained from the solutions obtained in the course of the study.

# Finding similar galaxies using deep learning methods

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We present the results of the application of automated clustering methods to a sample of galaxies images. The main goal is to develop a tool for finding galaxies, that are similar to a given one. Our purpose is to investigate methods of selecting and extracting comparable features of galaxy images. To achieve this goal we applied deep learning, in particular, autoencoder techniques.

Autoencoder is an unsupervised learning algorithm where a neural network is trained to copy its input to its output. In other words, it is trying to learn to approximate identity function, but with some constraints on the network, such as decreasing of the size of hidden layers, making it significantly less than input size, so we can reveal common patterns in data. Learning to reconstruct the input image from incomplete representation forces the autoencoder to detect the most important features of the data. For our problem, we are only interested in the hidden layer, which is represented by a vector. Using it as a marker of galaxy structure, shape, and other visual properties and comparing the measure of this vector we can reason about the similarity with other images.

We have applied this method to a sample of galaxies from Sloan Digital Sky Survey Data Release 14. On this stage of research, we selected galaxies with perceptible structure and large enough visible radius (around 7.5k images in total). All these images were used in training with augmentation (synthetically modified data) for dataset expansion. The current version of our software computes vector representation of galaxy and compares it with all other in demo database. It is worth noting that there are no robust methods that calculate likeness of content on two images except comparing by eyes. But our approach allows one to get an approximately similar galaxy, given properties such as class, shape, color, and other distinctive features. In the future, we plan to use another deep learning techniques and architecture to improve extraction and getting more explainable features. Also, this network can be applied and trained on a larger set of images.

# Investigation of carbon cycle gases local sources nearby the Peterhof station

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Carbon dioxide, methane and carbon oxide are the most important carbon cycle gases in Earth's atmosphere. So continuous monitoring of those mixing ratios in the ambient air is being carried out at the suburb of greater St. Petersburg site (Peterhof) since 2013. It gives us an opportunity to estimate the emissions of these gases, that is one of the prime interest for climate forecast.

For the estimation of $CH_4$, $CO_2$ and CO fluxes under nocturnal and calm conditions was used simple box model with consideration of absence of horizontal and vertical fluxes through boundaries of the box (based on the article of M.Zimnoch). Hence all income of gases due to emissions from earth surface of them remains in this box.

Average values of $CH_4$, $CO_2$ and CO fluxes estimated for Peterhof for 2014-2015 are of (44 ± 27), (10500 ± 7800) and (90 ± 100) t/($km^2$·yr), respectively. Mutual accumulation average values of $CH_4$, $CO_2$ and CO fluxes estimated for Peterhof for 2014-2015 at the same time are of (32 ± 45), (8500 ± 6300) and (28 ± 23) t/($km^2$·yr).

Thus analysis of the mutual accumulation of $CH_4$, $CO_2$ and CO allowed us to ascertain the main types of anthropogenic sources for the territory of Peterhof such as traffic, natural gas combustion in domestic appliances and industrial plants, residential heating located nearby the observational site (including wood burning during the cold season).

Investigation was supported by Russian Science Foundation (grant No14-17-00096) and Russian Foundation for Basic Research (grant No 18-05-000111). Authors thank Geomodel Research Center (SPbU) for providing the observational facilities.

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# Galaxies in deep fields. The methods of investigation of the structural parameters

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Investigation of the deep fields is one of the most efficient ways to study the evolution of the Universe. The prominent feature of the deep fields is that they allow to trace an object's evolution almost since its birth. The deep fields are long-exposure (starting with 0.1 yr) projects of detail exploration of small regions (~10 arcmin$^2$) on the celestial sphere. Redshifts that are typical for these projects are $z >> 0.1$. The number of detected objects is significant: thousands and tens of thousands for the most recent deep fields [1]. Thus, deep fields are a prolific source of observational material for investigation of galaxies, their morphology, and properties.

In this work, the asymmetry index of galaxies was investigated. The asymmetry index is a parameter that characterizes asymmetry of a galaxy's image. The index is determined as the difference of initial and rotated by 180 degrees images of a galaxy divided by the total luminosity of the galaxy.

The asymmetry of the galaxies that are located not too far from us (for instance, from Frei catalogue [2]) was investigated earlier [3, 4]. It was shown that the asymmetry index can play one of the most important roles in the creation of the new classification system for galaxies which can be used alongside with the Hubble's one.

For this particular work around 5000 galaxies were extracted (F814 and F606 filters were used) from the XDF. The analysis of the results was implemented. The main result is that the fainter the galaxy, the more asymmetric its shape.

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# Overview of Baikal-GVD neutrino telescope and it's effective areas calculation

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Baikal-GVD is a large-volume, kilometer-scale neutrino telescope under construction in Lake Baikal. It is designed to detect astrophysical neutrino fluxes at energies from a few TeV up to 100 PeV. The Baikal deep underwater neutrino telescope is an international project in the field of astroparticle physics and neutrino astronomy. The construction of the Baikal-GVD neutrino telescope is motivated by its discovery potential in astrophysics, cosmology and particle physics.

GVD is formed by multi-megaton subarrays (clusters). The full scale GVD will be an array of ~10000 light sensors with an instrumented volume of about 2 cubic km. The first phase (GVD-1) is planned to be completed by 2020-2021. It will comprise 8 clusters with 2304 light sensors in total.

The data analysis is a serious task for the collaboration. We use Monte-Carlo simulations to develop data processing algorithms, while raw data from the telescope is collected. This work contains a short overview at the project and shows Monte-Carlo estimation of the effective area of a one cluster of the telescope with different stages of the data processing flow.

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# On automated processing of photometric data

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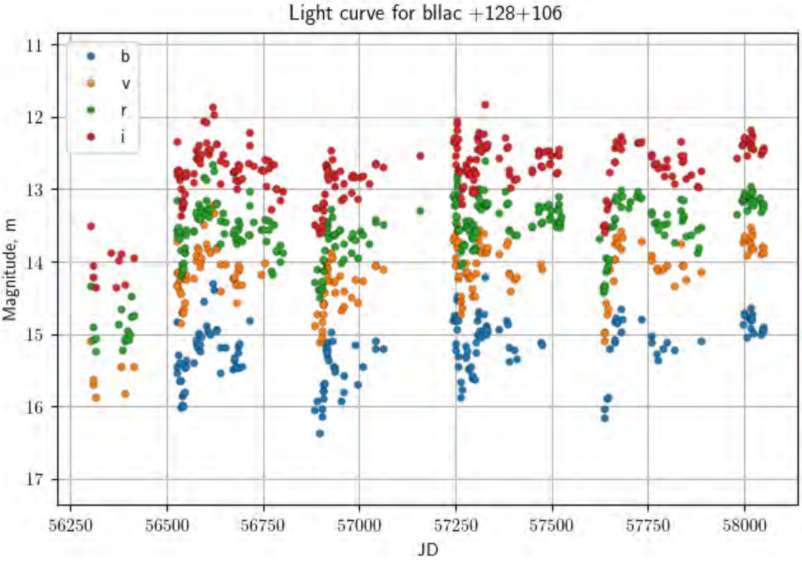
Active galactic nuclei (AGN) has been observed by the Department of Astrophysics of Saint Petersburg State University since 2005. A large amount of raw observational data was obtained during this time. However, it was not used fully: on the frames with the AGN there are some background stars, information about which we do not extract. Such work can not be done manually at any reasonable time.

To solve this problem, we developed an **aperPhot** package, which allows one to process all available observational data in a fully automated way. This package takes as an input a set of images and extracts photometrical parameters of every object on these images.

We applied this package to our entire data set and obtained database with light curves for all observed stars. Moreover, we developed utility **curvesMaker**, which allows us to store and analyze data more conveniently.



## References

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2. https://github.com/vadim-kravtsov/curvesMaker

# Geophysical survey for safety ensuring at the Mirny Station airfield, Eastern Antarctic

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Geophysical surveys are effective methods for non-destructive control and obtaining information about the geological environment. The work in the area of Mirny Station were planned as a continuation of an important project started in the 59th Russian Antarctic Expedition [1, 2], which implies the confirmation (or refutation) of the correctness of the choice of the landing site location. The main task was the joint use of georadiolocation (GPR) and seismic sounding. GPR is an electromagnetic method, and elastic waves are used in seismic sounding, so their joint application allows obtaining information about various properties of the medium.

In the course of work GPR profiling was performed at the set of profiles crossing aerodrome, and seismic work was done in its northern part. Comparison of GPR and seismic data obtained in one place showed that the methods reliably detect the same structures in the snow-firn cover. Their combined use ensures a more reliable interpretation. As a result of geophysical works some cracks were found on the surface, and it was decided to reduce the length of the airfield to 1,200 meters. From the other hand, lots of suspicious trails turned out to be safe and suitable for further use.

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# Velocity analysis based on data correlation

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Migration velocity analysis is based on an imaging condition and determinates the velocity model that optimally focuses the migrated image. Conventional wave equation migration uses only downward data propagation. Using complex velocity models gives rise to arrivals that are seen as noise in the imaged data. Reverse time migration propagates events both downward and upward through the velocity model, explicitly handling turning waves and all other complex propagation paths. We propose methods that measure the amount of focusing in the data domain and in the image domain for different types of migration.

The present study is focused on the impact of match of the used velocity model and the correct one on focusing/defocusing. Simple velocity model was considered. In the first case, focusing power based on energy density was estimated using exponential functional based on function of autocorrelation for different velocity models (see Fig. 1). In the second case, estimation of data misfit was produced using reverse time migration and conventional cross correlated imaging conditions (see Fig. 2).

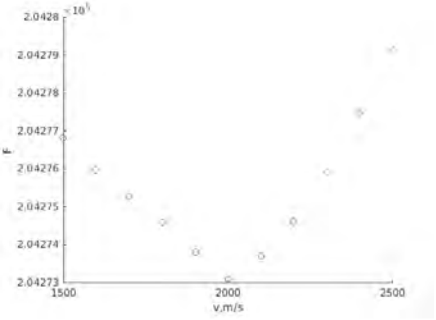

*Fig.1. Focusing power vs. velocity.*

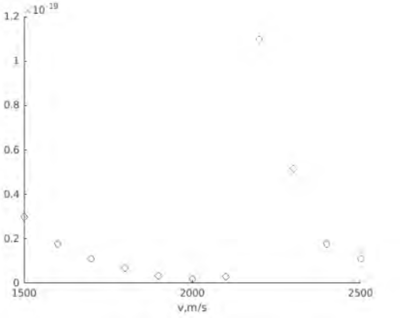

*Fig.2. Data misfit vs. velocity.*

As one can see from the figures minimizing the functionals allows to determine correct velocity model. It seems to be rational to apply this technique to complex synthetic data. Building of the velocity model is the next important task.

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# Structure of electromagnetic fields and plasma flows associated with time-dependent reconnection

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Magnetic reconnection is believed to be responsible for such explosive phenomena in space plasma, like solar flares and magnetospheric substorms. This process is associated with the decay of cosmic current layers, a sharp restructuring of magnetic field topology and the conversion of magnetic energy into kinetic and internal energy of the plasma. In this thesis we consider the process of time-dependent magnetic reconnection in a symmetric current sheet in the incompressible plasma model. For a given time-dependent electrical reconnection field, the shape of slow shocks, as well as plasma and magnetic fields in the whole space, are found [1]. In the Matlab environment, a program for visualization and computer animation of the magnetic reconnection process has been compiled for the cases of a single reconnection pulse, a double pulse, and the transition of the process to the stationary phase, which is described by the classical Petschek model [2].

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# Estimation of pitch angle of spiral galaxies using deep learning methods

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A pitch angle is a parameter that describes the overall shape of a spiral structure of a disk galaxy. It is defined as an angle between the spiral arm and the perpendicular to the radius vector drawn from the galaxy center. The pitch angle is an important parameter of a spiral galaxy, that is hard to estimate by an image automatically. The main purpose of our work is to create a tool based on a convolutional neural network that solves this problem.

A convolutional neural network consists of several convolutional layers. Each of them gets a multichannel image from the previous layer and convolves it with a mask. During the learning process, mask parameters evolve in order to decrease the loss function, which measures the error on images from the training set. Because of the local nature of convolution such networks are known to perform well in image processing. We also use dropout and batch normalization to avoid overfitting and exploding gradients problem, respectively.

Due to the lack of real labeled galaxies we use a set of synthetic images of galaxies with known pitch angle value to train our network. In the future we plan to additionally train our network on augmented real data, and then apply the trained network to a sample of images of real galaxies to estimate their pitch angle values.

# Effect of local gravity wave forcing on the circulation of the middle atmosphere

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A profound knowledge of atmospheric waves is essential to understand the processes in the middle atmosphere. The most important characteristic of waves is their ability to transport and deposit energy and momentum from their origin. In particular internal gravity waves (IGWs) distribute energy and momentum throughout the whole atmosphere thereby maintaining the circulation of the upper atmosphere. On the basis of density variance profiles derived from GPS radio occultation data a localized area of enhanced IGW breaking (Fig. 1) in the lower stratosphere over the East Asian region (32.5-62.5°N/118-169°E) has been discovered [1]. By using MUAM, a 3D mechanistic non-linear global circulation model for the middle and upper atmosphere, the impact of such a non-zonal IGW forcing on the stratospheric and mesospheric dynamics was examined. Depending on the intensity of the IGW hotspot additional planetary waves (PWs) are induced. The performance of a sensitivity study with regard to the spatial distribution of the IGW hotspot shows that the additional PWs can interfere destructively or even constructively with the at the lower boundary forced PWs in MUAM. Especially, with regard to the stability of the polar vortex the dynamics of the middle atmosphere is highly affected by these PWs.

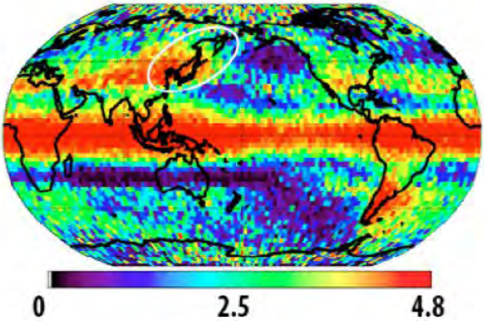

*Fig. 1. Annual mean of the potential energy in Jkg$^{-1}$ based on GPS Radio Occultation measurements averaged across the whole vertical profile for 2007-2010 [1].*

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# Photometric study of the young star PV Cep in outburst

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Subclasses of Sun-like eruptive young stars characterized by episodic outbursts in optic and infrared bands differ in the scale of outburst and their repeatability, spectral class and other features/ These are FU Orionis, EX Lupus, T Tauris, Ae/Be Herbig. Their research is important for understanding early stages of stellar evolution.

PV Cep is a star of type EX Lup, but it has some features, which make difficulties to define object class. According to observational data obtained in 2007-2017 (including the outburst in 2014-2017) on AZT-8 (Nauchny, Crimea) and LX-200 (Petrodvorets, Saint-Petersburg), we have analyzed the behavior of this star and tried to classify it.

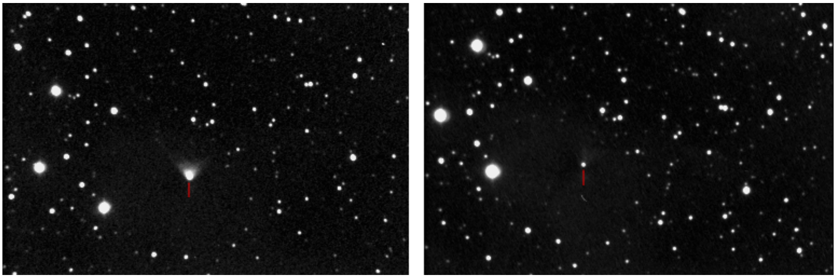

*Fig. 1. Image of PV Cep in the I band in 2015 (left) and 2007 (right), LX-200 (Saint-Petersburg).*

# C. Mathematics and Mechanics

# Old and New Results in Dimension Theory of Almost Periodic Dynamics

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We give an overview of old and present some new results concerning applications of dimension theory for studying almost periodic dynamics. One branch starts from a theorem of M.L. Cartwright [1], linking the topological dimension of the closure of almost periodic flows and the size of its frequency base. Cartwright's approach was extended by R.A. Schmidt (for ODE's, [2]) and J. Mallet-Paret for (DDE's, [3]). In [4] K. Naito studied fractal dimensions of forced almost periodic oscillations, using Diophantine approximations. His approach was systemized and extended by M.M. Anikushin in [5,6]. We will show how the latter approach can be applied to study forced almost periodic oscillations in the class of control systems in $\mathbb{R}^n$:

$$\dot{u} = Au + d\varphi(\sigma) + f(t), \sigma = c^* u.$$

For this class I.M. Burkin and V.A. Yakubovich, using a method of M.A. Krasnoselskii, have obtained frequency-domain conditions for the existence of two almost periodic solutions, one of which is exponentially stable. It turns out that within these conditions it is possible to obtain some dimension estimates.

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# Modeling of functional and mechanical behavior of CuAlNi-based shape memory alloys

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The Cu-based shape memory alloys (SMAs) such as CuAlNi are promising for design of actuators and vibration protection devices due to complete deformation recovery and narrow temperature hysteresis of martensitic transformation. For successful and reliable application of Cu-based SMAs as well as for the prediction of new properties one needs both experimental studies and models allowing calculation of mechanical behavior in various temperature and stress conditions. Nevertheless, there are known only a few models describing mechanical behavior of these materials. This fact determines the topicality of the present work that is devoted to modeling of functional and mechanical properties of CuAlNi SMAs.

The deformation matrix for the martensitic transformation β1(DO3)-β1'(18R) is calculated and the crystallographic resource is determined. The anisotropy of elastic constants in the austenite phase is taken into account, matrices of elastic constants and elastic compliances based on the experimental work [1] are written out. Modeling of isothermal deformation of single crystals of different orientations in the austenite state is performed when the SMA demonstrates pseudoelasticity (Fig. 1). The obtained results are in good agreement with available experimental data.

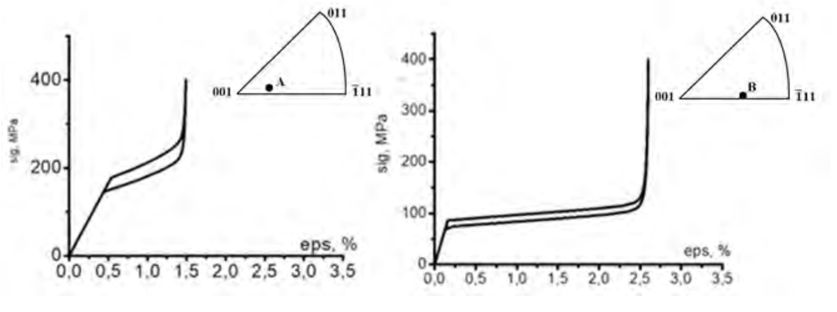

*Fig. 1. Stress-strain curves for CuAlNi single crystals of different orientations.*

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# Using reservoir computing to reconstruct the dynamics of cell shape and orientation

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Recurrent Neural Networks (RNNs) are a class of neural networks, which contains cycles. These networks are useful because they can approximate dynamical systems. In 2001 a fundamentally new approach to RNN design and training was proposed by Wolfgang Maass and Herbert Jaeger [1]. Now this approach often is called Reservoir Computer Paradigm (Fig. 1).

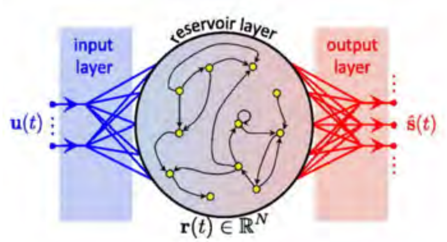

*Fig. 1. A reservoir computer.*

This paradigm was applied by us to research some chaotic dynamical systems with attractors. The first way, which was realized, allows to replicate chaotic attractors using network by training it during some period, and then we taking the outputs as an input (Fig. 2).

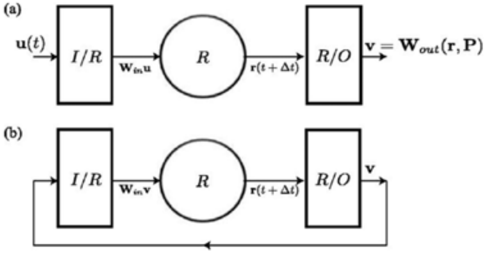

*Fig. 2. Configurations in the training (a) and the prediction (b) phase.*

Another way allows to deduce the state of a dynamical system from a limited number of concurrent system state measurements. These two methods were used on a set of data obtained by observation of spontaneously migrating *Dictyostelium* cells [2].

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# About stability loss of zero solution in one boundary-value problem

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Let us consider one boundary-value problem with linear deviate in enge condition

$$u' = \ddot{u} + \gamma u - u^3 \tag{1}$$

$$u'(0,t) = 0, \; u'(1,t) = \alpha u(x_0, t), \tag{2}$$

where $\alpha, \gamma \epsilon \mathbb{R}$, $x_0 \in [0,1]$.

Boundary-value problem (1), (2) has the trivial solution. Depending on the values of parameters, this balance state might be stable or unstable. The main ways of stability loss of trivial solution are divergent, when a zero appears in the stability spectrum of balance state, and oscillating, when a pair of eigenvalues appears on imaginary axis of complex plane. Our task was to find critical values of initial parameters *α* and γ, when there is the stability loss of trivial solution of boundary-value problem (1), (2).

For the task there were used analytical and numerical methods of research. For numerical research of oscillating stability loss of zero balance state there was considered a chain of *n* connected oscillators, which simulates boundary-value problem (1), (2)

$$\dot{u_j} = n^2\left(u_{j+1} - 2u_j + u_{j-1}\right) + \gamma u_j - u_j^3 \tag{3}$$

$$u_0 = u_1, \;\; u_{n+1} = u_n + \frac{\alpha}{n} u_k, \tag{4}$$

Index $k \in [1;\, n]$ of oscillator $u_k$ is determined proceeding from shift $x_0$ in boundary condition (2).

The numerical research was carried out by means of special software. All calculations were performed on a large number of independent streams of CPU.

As a result there were found some critical values of initial parameters *α* and γ, when zero balance state of problem (3), (4) lost its stability. In addition for divergent and oscillating of stability loss there were constructed equations for the amplitude of oscillations of zero balance state of linearized problem (1), (2).

This work was supported by the Russian Science Foundation (project nos. №14-21-00158).

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# Bifurcations of Solutions in a Single Equation from Nonlinear Optics

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We consider a periodic boundary-value problem for optical system with feedback described by parabolic functional differential equation with space delay

$$u_t + u = d\,u_{xx} + K\,(1 + \gamma \cos u_h), \quad u_h = u(t, x + h),$$
$$u(t, x) = u(t, x + 2\pi).$$

Solvability of this problem was studied in the works by P.E. Sobolevsky, and this method assumes to use the analytical theory of semigroups of bounded linear operators.

In order to solve the occurring bifurcation problems there were used the investigation methods of dynamical systems with an infinite-dimensional phase space (a space of initial conditions) such as: the method of integral manifolds, the method of Poincare–Dulac normal forms and asymptotic methods of analysis.

Both possible in the given situation problems were studied: in codimension one and in codimension two. The analysis of normal form was given. In particular, asymptotic formulas were obtained for nonhomogeneous wave solutions. The question about the stability of these solutions was studied.

The stated boundary problem was studied in a number of papers (for example, [1-3]), but under different assumptions, in a different formulation.

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# On Properties of Solutions of Delayed Maxwell's System with a Thermal Effect

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We study a problem arising from microwave heating with a delay in the electrical conductivity. The mathematical model consists of Maxwell's system coupled with heat the equation and forms the following system:

$$
\begin{array}{lr}
\varepsilon(x)E_t + \sigma\big(\theta(x,t-h)\big)E = \nabla \times H, & (x,t) \in \Omega \times [0,T], \\
\mu(x)H_t + \nabla \times E = 0, & (x,t) \in \Omega \times [0,T], \\
\theta_t - \nabla \cdot [k(x,\theta)\nabla\theta] = \sigma\big(\theta(x,t-h)\big)|E|^2, & (x,t) \in \Omega \times [0,T], \\
v \times E(x,t) = v \times G(x,t), & (x,t) \in \partial(\Omega \times [0,T]), \\
\theta_v(x,t) = 0, & (x,t) \in \partial(\Omega \times [0,T]), \\
E(x,0) = E_0(x), \quad H(x,0) = H_0(x), & x \in \Omega, \\
\theta(x,s) = \theta_0(x,s), & (x,s) \in \Omega \times [-h,0].
\end{array}
$$

Here $\Omega$ is a domain in $\mathbb{R}^3$, $E(x,t)$ and $H(x,t)$ denote the electric and the magnetic fields, $\theta(x,t)$ is the temperature, $h > 0$ is the delay time, $\varepsilon(x)$, $\sigma(\theta)$, $\mu(x)$ are the electric permittivity, the electric conductivity and the magnetic permeability, respectively. This problem (with no delay) was studied in [1, 2]. In [3] we extended some of these results, such as existence, uniqueness, boundedness and continuous dependence on intial conditions, to the system with delay.

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# Bifurcations in a cardiac conduction system with discrete time and the use of control

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The talk describes a cardiac conduction system model including a piecewise smooth map [1]. The main focus of the study is on finding such values of the model parameters that correspond to cardiac conduction failures and on the ways to prevent these failures. A typical failure is the occurrence of oscillations between the two values in the nodal conduction time when the heart is beating. This suggests that there is an occurrence of a period doubling bifurcation. To prevent such dangerous states, a feedback control is required. In our model, according to [2], a feedback control is introduced in the cardiac conduction system. In addition, we consider a model with an additional deformation parameter. We prove the continuous dependence of the fixed point of the deformed map on the deformation parameter and, as a consequence, the convergence of the fixed point of the deformed map to the fixed point of the original map as the deformation parameter tends to zero. For the cardiac conduction system, a normal form of a period doubling bifurcation for piecewise smooth maps is obtained.

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# Stability conditions of the one nonlinear boundary-value problem in theory of elastic stability

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In this paper we consider a nonlinear boundary-value problem

$$u_{tt} + (g_1 u_t + g_2 u_{t,xxxx}) + (1 - i\omega)u_{xxxx} = F(u_x, u_{xx}, u_{tx}) \qquad (1)$$

$$u(t,0) = u(t,1) = u_{xx}(t,0) = u_{xx}(t,1) = 0 \qquad (2)$$

where $u = u_1(t,x) + iu_2(t,x)$ – complex-valued function. In this case

$$F(u_x, u_{xx}, u_{tx}) = u_{xx}\left(a_1 \int_0^1 |u_x|^2 dx + a_2 \frac{d}{dt} \int_0^1 |u_x|^2 dx\right)$$

Finally, $g_1$, $g_2$, $a_1$, $a_2$ are some positive constants. This problem arises in the theory of elastic stable and describes the transverse vibrations of rotating rotor of a constant cross-section from a viscoelastic material whose ends are pivotally fixed. Control parameter ω is the normalized rotation speed (f.e., [1-2]). The problem (1), (2) has zero equilibrium state. Thus, the following statement is true.

**Lemma 1**. The solution $u \equiv 0$ is asymptotically stable, if $\omega < \omega_0$ and loses stability at $\omega > \omega_0$. At $\omega = \omega_0$ the critical case is realized.

In this situation $\omega_0 = \min \omega_k$, where $k=1,2\ldots$ and

$$\omega_k = \frac{g_1 + g_2(\pi k)^4}{(\pi k)^2}.$$

**Theorem 1.** Let $\omega > \omega_0$. The boundary problem (1), (2) has the nontrivial self-similar periodic solution in the form

$$u_m(t,x) = \eta_m \exp(i\sigma_m t)\sin(\pi m x), \qquad (3)$$

where m is natural number and

$$\eta_m{}^2 = \frac{2(\omega^2 - \omega_m{}^2)}{a_1 \omega_m{}^2}, \sigma_m = \omega \frac{(\pi m)^4}{g_1 + g_2(\pi m)^4}.$$

The solution (3) is asymptotically stable, if $g_1 < g_2 R$, if $m < n$ and $g_1 > g_2 R$ in case $m > n$, where

$$R = R_{m,n} = \frac{m^3 n^3}{n^2 + m \ \ + m^2}\pi^4.$$

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# D. Solid State Physics

# Secondary electron emission from thin insulating films under the irradiation of helium ion beam

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Helium ion microscope (HeIM) is a functional scientific tool, which uses secondary electrons (SE) excited by focused helium ion beam for imaging of the surface morphology and characterization of the materials structure and electronic properties [1]. Besides, several technologies such as ion beam induced deposition and sub-nanometer ion beam lithography were implemented with HeIM. The efficiency of these processes depends on the parameters of SE emission, such as the secondary electron yield and the secondary electron energy distribution (SEED). However, the influence of positively charged ions on insulators leads to the charge accumulation in the sample that distorts the results of investigations and worsens the resolution of lithography. Thus, new HeIM techniques free of the charge effect are required for investigation of insulators.

In this work, we described a special measurement technique developed for the investigation of insulating materials in HeIM. SE emission from thin insulating films was investigated with the scanning helium ion microscope Zeiss ORION. The dependence of the SE signal on the sample bias voltage was measured by means of the retarding potential method [2] in the absence of positive charge accumulation. Reliable SEED data for silicon dioxide, silicon nitride and poly(methyl methacrylate) thin films were obtained.

In addition, the dependence of the surface potential on the number of implanted ions was obtained by comparison of the dependence of the SE signal on the number of ions and the dependence of the SE signal on the retarding voltage. The experimental results qualitatively agree with the simulation results obtained for $SiO_2$ in [3-5].

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# Excitons in ZnO quantum wells

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Zinc oxide is a promising semiconductor for various applications. Its properties are similar to those of gallium nitride, which has already become an indispensable material in optoelectronics. It is worth to be noticing that the technology of ZnO-based structures is simpler and the quality of these structures is better as compared to GaN. In recent years, ZnO has been actively studied in connection with the prospect of giving it the new properties.

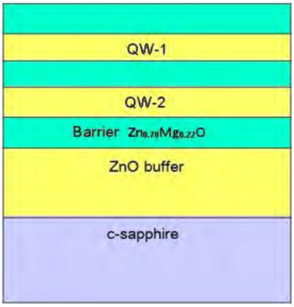

*Fig. 1. The structure contains two quantum wells of the thicknesses 2.7nm (QW1) and 7.1nm (QW2).*

The ZnO/ZnMgO heterostructure with two ZnO quantum wells of the thicknesses 2.7 nm and 7.1 nm grown with the moleculalbeam epitaxy (MBE) method in the direction of the polar axis is under our investigation (Fig. 1). We have studied the luminescence and reflection spectra (Fig. 2) in the temperature range 5 – 200 K under the different excitation conditions.

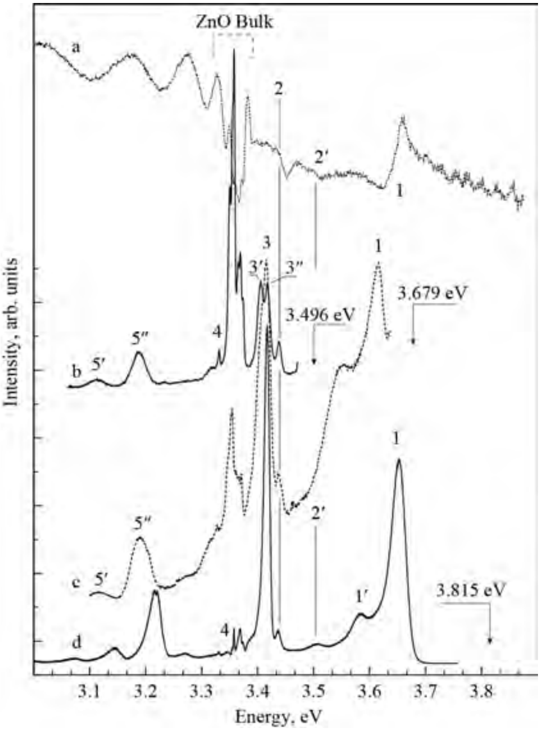

*Fig. 2. The reflection spectrum (a) and the luminescence spectra (b – d) of the ZnO / $Zn_{0.78}Mg_{0.22}O$ structure at the different exciting photon energies. T = 5K.*

The details of the observed structure have been identified. It is shown the piezoelectric field does not contribute significantly in the energies of the optical transitions.

# DFT study of hydrogen localization and mobility in V-Pd alloys

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V-Pd alloys are the promising materials for hydrogen separation. Being much cheaper than pure Pd they exhibit comparable efficiency [1]. According to experimental studies alloying Pd V moderates the hydrogen solubility, which is too high in pure V [2], but alloys are still characterized by high hydrogen diffusivity. To understand the observed phenomena at the microscopic level theoretical studies are highly required.

In this contribution we report on the results of the calculations carried out within the plane-wave pseudo-potential density functional theory (PWP DFT) method using the Perdew–Burke–Ernzerhof generalized gradient approximations for exchange-correlation potential and the ultrasoft Vanderbilt pseudopotentials as implemented in the Quantum Espresso package. The kinetic energy cutoffs for wave functions and charge density expansion were taken 60 and 360 Ry, respectively.

We considered the body-centered cubic $V_{16-n}Pd_n$ and $V_{16-n}Pd_nH$ supercells containing 16 metal and 1 H atom, with n = 0, 1, 2 and 3. For n = 2 and 3, mutual arrangements of Pd atoms were found. The calculations confirmed that solubility energy of hydrogen in the $V_{13}Pd_3H_1$ supercell is 0.15 eV lower than in $V_{16}H$.

The study of hydrogen localization in $V_{16-n}Pd_nH$ revealed that in pure BCC vanadium H occupies tetrahedral interstitial sites, while octahedral ones are unstable. The partial substitution V for Pd leads to: (i) hydrogen avoids first coordination sphere of Pd; (ii) octahedral sites become metastable. All this together changes hydrogen diffusion mechanisms and pathways. In particular, the activation energy of hydrogen motion decrease from 0.14 eV in pure vanadium to 0.06 eV in $V_{13}Pd_3H_1$ supercell.

The calculations were carried out using computational facilities provided by Resource Center «Computer Center of SPbU» (http://cc.spbu.ru/en).

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# Optical study of GaP:N heterostructures

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Gallium Phosphide is a wide bandgap semiconductor with a cubic crystal structure and an indirect bandgap structure. A lot of attention is directed to the study of this material due to its unique properties. By several opinions this material (1), in the case of addition isoelectronic compound Nitrogen, is better described as heavily doped semiconductors rather than as isoelectronic alloys. Among several technological applications like GaP nanowires which are used for bio-applications, doped GaP is usually used in light emitting diodes that emit wavelengths in the visible range from red to green. The structure and properties of this material are not fully studied and can hide a lot more for progress. That is why the study of this material is so important.

Our sample was grown via Molecular-beam epitaxy (MBE) (Fig. 1).

Refraction, photoluminescence and temperature dependence were measured. On the photoluminescence spectra we found acoustic and optical phonon's replica (Fig. 2) which are similar to the results previously obtained by a group of scientists in 2017 [1].

In this work we will discuss samples grown by MBE and low pressure metal-organic chemical vapour deposition (MOCVD).

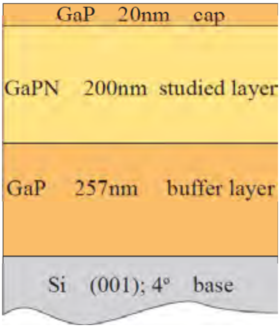

*Fig. 1. Sample architecture.*

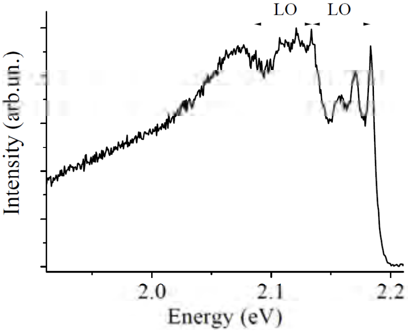

*Fig. 2. Spectrum of sample.*

The authors acknowledge support from a grant the Ministry of Science and Education 16.2593.2017/4.6.

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# Estimation of the Dirac point band gap in topological insulators doped with the transition and rare-earth metals

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In recent years numerous of works have been devoted to studying of magnetically doped topological insulators (TIs) due to emergence of the quantum anomalous Hall effect (QAHE). Realization of the QAHE is required opening of the magnetically induced band gap at the Fermi level with formation of the chiral edge states inside this gap. Although, general mechanism of transition to state of the QAHE is well described, proper understanding and controlling of the influence of magnetic dopant on emergence of the QAHE are assumed feather systematic investigation [1]. In the present work we gave attention to the such one main aspect of realization of the QAHE as the Dirac point band gap opening. With this intention we explored electronic structure of the Dirac cone and magnetic properties in $(Bi,Sb)_xTe_3$ doped with transition metals (TM) $V_{(2-x)}$ and rare-earth metals (REM) $Gd_{(2-x)}$. Dopants we studied possess different magnetic moment which can be applied for gently variation of internal magnetic moment and induced band gap. It is believed that doping of TIs with REM is more beneficial since magnetic TM are usually divalent and act also as electric dopants [2]. REM are trivalent and has an equal number of bonding electrons to Bi (Sb), therefore, only magnetic moment can be induced.

For analysis of the samples we have used several methods such as angular resolved photoemission spectroscopy (ARPES) and resonance PES. ARPES with high resolution has been applied for the band gap investigation. For the following treatment we have used approach with modeling of experimental spectra. It allows to reduce features appeared during measurements and make more correct estimation of the band gap. Resonant PES has been used to match the location and contribution of the bands of the magnetic impurities in PES spectra hereby has given information of their bonding with atoms of TI.

Based on these experimental measurements we have examined origin of the band gap opening in magnetically doped TIs. Either we will show changing of the band gap related to the element of magnetic impurity. As one of the ways of the Dirac point gap modification role of the 2D surface Dirac-fermion-mediated magnetic coupling will be discussed [3].

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# Electronic structure of graphene on Re(0001) intercalated with Bi atoms

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In the last decade graphene had been established as the one of the most interesting material for researchers, due to the linear dispersion of electronic states, the so-called Dirac cone. Owing to its two-dimensional crystal structure, graphene properties strongly depend on the interaction with the various types of substrates. For example graphene on Ir(111) or Pr(111) is quasi-free-standing, while in the case of Re(0001) substrate graphene has a strong interaction with this surface. For such a system the Dirac cone collapses, and dispersion near the high-symmetric K-point is no longer linear, as in the quasi-free-standing graphene. Nevertheless, by intercalation of different atoms under graphene, such as Au, Al or Bi [1,2] we can detach it from the substrate and reduce the interaction between graphene and the metal surface. The Dirac cone is expected to restore after the intercalation, but the charge transfer and local hybridization effects may still modify the ideal linear Dirac cone structure.

This work is devoted to the experimental study of the electronic structure of graphene/Re(0001) after the Bi atoms intercalation. The data had been obtained by means of angle-resolved photoemission spectroscopy with the photon energies of 21.2 and 40 eV. The experiment had been performed at research resource center "Physical methods of surface investigations".

Our results demonstrate that the unique linear dispersion is indeed restored after Bi atoms intercalation. Moreover, the Dirac point position is found to be different depending on the intercalated atoms configuration. There are two Dirac cones in the ARPES image and for the first one the charge transfer from the Bi atoms leads to the Dirac point position below the Fermi level, i.e. to the n-doping of graphene. For the second one the Dirac point is located above the Fermi level resulting in p-doping. Possible reasons of this behavior as well as the perspectives of such graphene p-n junction will be discussed.

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# Reaching low temperatures of GaAs crystals via a combination of optical and magnetic cooling of the nuclear spin system

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Modern cryostats allows temperatures in the millikelvin range to be reached. However, this appears to be the limit of conventional cryostats, and is precisely the reason why the investigation of other cooling techniques is important.

Optical orientation of paramagnetic nuclei lowers the temperature of the spin system [1], which can be lowered further via adiabatic demagnetization [2]. This system then interacts thermally with the lattice, and eventually equilibrium is reached.

Here we present a theoretical estimate of the dependence of equilibrium temperature with respect to the initial temperature of the bulk crystal, which was assumed to lie in the range from several K to the millikelvins. The calculations were carried out with several assumptions, the main one being that the crystal consists only of the lattice and the nuclei, meaning that electons were assumed to have zero heat capacity; another assumption was that the lattice heat capacity follows the Debye $T^3$ law.

It was found that if the lattice initially has a temperature of 1 mK it may be possible to cool the whole crystal down to the temperature of the nuclear spin system, which is around $10^{-6}$ - $10^{-7}$ K.

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# The formation of nanostructures by means of local ion beam enhanced etching

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Ion beam treatment is a commonly used procedure in microelectronics for modification of material properties, including the etching rate. In the paper [1] we have estimated the dependence of the etching rate of irradiated areas of $SiO_2$ on the concentration of ion induced defects. New promising method to fabricate nanostructures can be developed with help of this effect of selective etching.

In this work we irradiated closely spaced rectangular areas with various distances between them by means of the helium ion microscope. Ion scattering in the matter leads to the defect formation and subsequent enhanced etching in the volume close to irradiated region. After etching we measured distances between such etched away volumes by means of the scanning electron microscopy (SEM). Using Monte-Carlo simulation [2] and previously obtained dependence of the etching rate on defects concentration we suggest theoretical models of the etching near the boundary of irradiated area. As a result of the etching of closely spaced irradiated areas the nanostructure such as a string fixed at both ends can be formed (Fig. 1).

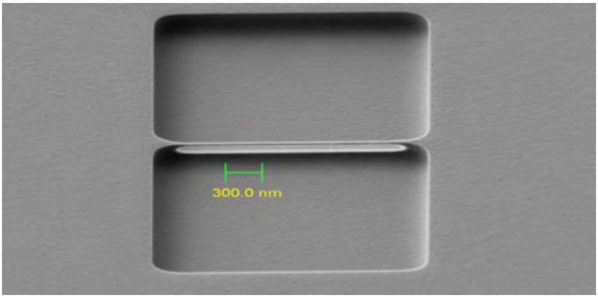

*Fig. 1. SEM image of the nanostructure such as a string fixed at both ends by means of ion beam enhanced etching.*

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# NEXAFS study of electronic structure of $Al_8Co_{17}Cr_{17}Cu_8Fe_{17}Ni_{33}$ compositionally complex alloy

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Compositionally complex alloy (CCA) is a new class of materials being a subjected for an intensive investigation all over the world in last decade. Many of CCA show exceptional properties, including high strengths at elevated temperatures, ductility, toughness, resistance to corrosion, wear and fatigue [1].

The knowledge of electronic structure is a basic prerequisite for understanding of physical, chemical, mechanical and thermodynamic properties of CCA [2]. Information on the influence of valence electron concentration on the phase stability is extremely important for alloy design and for controlling the mechanical behavior [3,4].

In the presented work, electronic structure of $Al_8Co_{17}Cr_{17}Cu_8Fe_{17}Ni_{33}$ CCA has been studied by soft X-ray absorption spectroscopy by measuring near edge absorption fine structure (NEXAFS) in the vicinity of $L_{2,3}$ edges of Fe, Co, and Ni in $Al_8Co_{17}Cr_{17}Cu_8Fe_{17}Ni_{33}$ and in the corresponding pure metals. The occupancy of the 3d shells of Fe, Co and Ni in $Al_8Co_{17}Cr_{17}Cu_8Fe_{17}Ni_{33}$ has been determined from the normalized intensities of the spectra. The influence of the alloying elements and the crystal structure on the electronic structure of Fe, Co and Ni in $Al_8Co_{17}Cr_{17}Cu_8Fe_{17}Ni_{33}$, such as d shell occupancy and branching ratio, has been analyzed. The absorption spectrum of Ni in $Al_8Co_{17}Cr_{17}Cu_8Fe_{17}Ni_{33}$ is shifted to higher energy by 0.6 eV compared to that in pure Ni. This shift is ascribed to higher binding energy of Ni in $Al_8Co_{17}Cr_{17}Cu_8Fe_{17}Ni_{33}$ compared to pure Ni or to a shift in the electronic density of empty Ni 3d states.

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# Analysis of temperature programmed desorption spectra of CO photooxidation products and $CO_2$ on $TiO_2$ surface

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The photocatalytic oxidation by $TiO_2$ has attracted much interest due to its important role in the transformation and decomposition of organic compounds. The photooxidation of CO on $TiO_2$ is considered as the simplest reaction to study processes on catalysts surface. Earlier it had been shown that the products of CO photooxidation on $TiO_2$ remains on the surface predominantly as carbonate $CO_3$ and may be removed (as $CO_2$) by heating up to 500 K [1]. In present work TPD spectra of $CO_2$, remaining on the dehydroxylated $TiO_2$ rutile surface after the adsorption of $CO_2$ and after UV-VIS irradiation of titania in CO – $O_2$ mixture, are compared and analyzed.

Main TPD peak of strongly bonded carbonate $CO_3$ species is considered as monomolecular desorption with two types of precursor states: 1) “over an empty site” and 2) “over a filled site” (Fig. 1). Basing on the temperature dependence of the effectiveness of carbonate species production during $CO_2$ adsorption a feature of potential energy curve of $CO_3$ on $TiO_2$ rutile surface is revealed.

The present study was performed within the Project “Establishment of the Laboratory of Photoactive Nanocomposite Materials” financed by a Grant (No. 14.Z50.31.0016) from the Government of the Russian Federation. We are grateful to the Resource Centers “Nanophotonics”, “Centre for X-ray diffraction Studies” and “Centre for Innovative Technologies of Composite Nanomaterials” of St. Petersburg State University for the sample characterization.

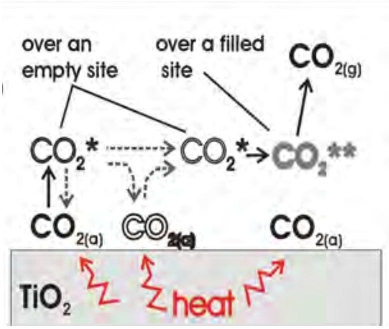

*Fig. 1. The model of $CO_2$ desorption from $TiO_2$ surface.*

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# Superconductivity in confined Ga-Ag alloy

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Nowadays thanks to a large variety of possible applications, superconductivity in nanostructures is of great interest to modern scientific community. A significant amount of new interesting information about superconductivity of pure metals embedded into porous matrices was obtained [1]. Still the full understanding of superconductivity in metallic eutectic alloys in nanostructures has not been achieved yet.

For this research the porous glass with 7 nm mean pore size filled with the Ga-Ag eutectic alloy was used. Then the dc and ac magnetizations were observed within a temperature range of 1.9-10 K in magnetic fields from 0 to 9 T measured by Quantum Design MPMS 3 and PPMS-9. For ac magnetization measurements the dependences on the amplitude of ac field and on the frequency range from 90 Hz to 7 kHz were investigated (Fig. 1). The observed temperature and frequency dependencies of the real and imaginary parts of ac and dc magnetizations were used to plot a T-H phase diagram, which revealed an anomalous positive curvature of the critical lines at low magnetic fields. This anomaly could be explained by structural changes in the vortex system under nanoconfinement that leads to a shortened correlation length.

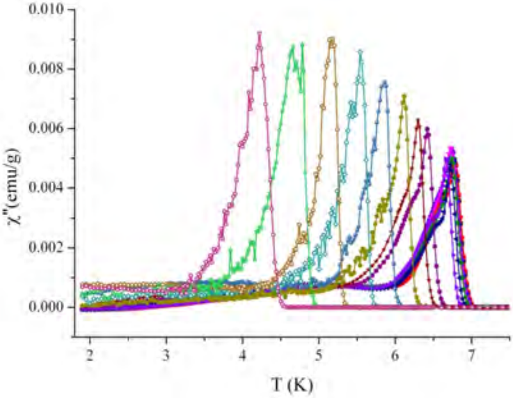

*Fig. 1. The temperature dependence of the imaginary part of the ac susceptibility at the frequency of driving field 1 kHz and the amplitude 1 Oe.*

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# Electronic structure of topological insulator $Bi_{1.09}Gd_{0.06}Sb_{0.85}Te_3$

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The search of new materials with special electronic properties is processing nowadays. Topological insulators are one of such materials with huge perspectives for practical applications. Their main unique feature is the Dirac cone formed by topological surface states. Topologically protected surface electrons cannot be scattered by defects or other environmental disturbance. That is why resistance of the media is insufficient to interfere with electron motion [1].

Nevertheless, it is necessary to have a possibility to control the Dirac cone structure for using these materials in devices. The most studied compounds of topological insulators are bismuth chalcogenides. To solve the problem of Dirac point position controlling the atoms of other metals (Sb) can be added in stoichiometry. On the other hand, we can change electronic structure of the Dirac cone by doping by magnetic metal atoms. As a result, band-gap appears in electronic structure of the Dirac cone and the system goes into condition of quantum anomalous hall effect [2]. The systems doped with transition metals have been studied recently. However, the most interesting is doping by rare-earth metals, for example, Gd. Gd has large magnetic moment and large atomic number, therefore spin-orbit coupling does not decrease upon the doping.

This work is devoted to study electronic structure of topological insulator with $Bi_{1.09}Gd_{0.06}Sb_{0.85}Te_3$ stoichiometry which is characterized by Dirac point position near the Fermi level and large doping concentration of rare-earth magnetic metal. The study was carried out using angle-resolved photoemission spectroscopy. Besides the studying of the clean surface of this compound we have investigated the influence of the residual gas molecules adsorption on the electronic structure. The obtained results indicate the presence of a shift of the Dirac point depending on the exposure time and temperature. Potential causes for this behavior will be discussed in current work.

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# NEXAFS study of composite Cu/MWCNT

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Surface decorating of multi walled carbon nanotubes (MWCNT) with nanoscale metal-containing particles gives them unique physical and chemical properties and leads to the creation of new composite materials. Such materials have a great prospect of application in many areas. In particular, the composite based on MWCNT modified with copper nanoparticles is used as a catalyst in a reduction process of germanium tetrachloride with hydrogen [1].

This paper discusses the results of composite Cu/MWCNT studies by Near Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy, X-Ray diffractometry (XRD) and scanning electron microscopy (SEM) methods.

The composite MWCNT/Cu was prepared by the metal organic chemical vapor deposition (MOCVD) growth technique using copper formate as a pyrolytic Cu source. Previously we have used this technique to form coating on the MWCNT surface for pyrolytic chromium [2].

SEM method has shown that copper is deposited on the MWCNT surface in the nanoparticles form. According to diffractometry data it was found that the substance of copper-containing nanoparticles is the cooper with cuprous oxide $Cu_2O$ admixture. NEXAFS study of the pristine MWCNT and composite Cu/MWCNT was carried out in the C1s- and Cu2p-absorption edges using synchrotron radiation of RGBL at BESSY II. The NEXAFS C1s-spectra analysis has shown that nanotubes surface is not destroyed, but it is modified due to the single, double and epoxy carbon-oxygen bonds. Based on the NEXAFS Cu2p-spectra data, it was suggested that the copper oxide CuO is formed on the copper nanoparticles surface.

This work was supported by grants RFBR and Ministry of Economy of the Komi Republic №16-42-110610, 16-43-110350; Russian-German Laboratory at BESSY II; Program of the fundamental researches of UrB RAS № 18-10-2-23.

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# Manipulation of electronic structure of graphene grown on Ir(111) and Pt(111) via adsorption and intercalation of different metal atoms

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Graphene is a two-dimensional hexagonal crystal structure composed of carbon atoms. Unique electronic properties of graphene make it appealing for nanoelectronics [1]. The dispersion dependence in graphene near the Dirac point has a linear nature, so that electrons and holes in graphene move like massless particles (for example photons). It is possible due to graphene's crystal structure consisting of two equivalent sublattices A and B.

The properties of graphene on various substrates are different from those for the free-standing graphene. For example, graphene is p-doped on Pt(111) and Ir(111) substrates, it means that the Dirac point lies above the Fermi level. Adsorption and intercalation of different metal atoms (Pb, Gd, Na) can be used for manipulation of graphene electronic structure [2,3]. So, Pb, Gd and Na atoms shift the Dirac point below the Fermi level, i.e. they make the system n-doped.

In this work we studied several systems with graphene: graphene on iridium before and after lead intercalation, graphene on platinum before and after gadolinium intercalation and graphene on platinum before and after sodium adsorption. The obtained systems were studied by angle-resolved photoemission spectroscopy (ARPES) and low energy electron difraction (LEED). Our results show the possibility of effective tuning of the Dirac point position and band gap value by intercalation(adsorption) of different metals underneath(on) graphene.

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# Coexistence of phases and hysteresis of phase transition in $MAPbI_3$ single crystal revealed by photoluminescence spectroscopy

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In this work, the temperature behavior of the photoluminescence spectra of the hybrid halide perovskite $MAPbI_3$ in the temperature range of 3.6–180 K is investigated. Of particular interest is the phase transition between the tetragonal and orthorhombic phase near 163 K [1]. An analysis of the photoluminescence spectra in the temperature range of 130–170 K (Fig. 1) shows the presence of two peaks corresponding to the recombination of excitons in the crystal regions with different phases [2].

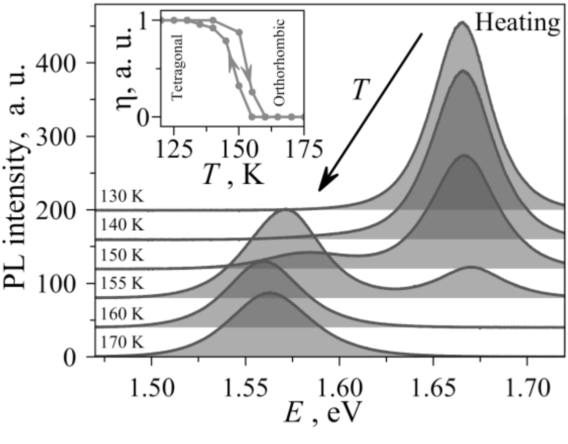

*Fig. 1. Temperature dependence of the photoluminescence spectra. Inset shows the dependence of the order parameter η on temperature during cooling and heating.*

During the heating and cooling the energy position of these peaks *E* and the order parameter *η* (the ratio of the intensity of one peak to the total intensity of the two) do not coincide, which indicates a hysteresis of the phase transition.

Thus, photoluminescence spectroscopy could be used for observation of structural transformations of halide perovskite crystal.

The work was carried out by the equipment of St. Petersburg State University resource center “Nanophotonics”.

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# NEXAFS study of fish and mammals bone

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Bone is a complex hierarchically organized composite material comprising both organic (primarily collagen) and inorganic (bioapatite or hydroxyapatite (HA), $Ca_{10}(PO_4)_3(OH)_2$) components, as well as lipids and water. Bioapatite is a unique mineral phase characterized by very small (~50x25x5nm) crystals, low OH-content and poor crystallinity. Bone hierarchical structure may be represented in the form of 3D-super-lattice (3DSL) where apatite nanocrystallites with average size L separated by hydrated layers with d thickness [1].

Recently we have investigated the atomic, chemical and mineral composition and bone hierarchical structure of Antarctic Ice Fishes hard tissue and mineralized formation particularly bone, otholites, scales and teeth by NEXAFS (Near Edge X-Ray Absorption Fine Structure) spectroscopy for the first time [2]. Current study is extended this investigation to wide class of fish and mammalian hard tissue.

All NEXAFS C1s-, N1s-, F1s-, P2p-, and Ca2p-spectra were measured in total electron yield (TEY) mode with high accuracy energy calibration at synchrotron source BESSY II using radiation from the Russian-German dipole beamline [3].

This work was supported by the Program of UB RAS №18-10-2-23; grants RFBR and KR 16-42-110610 p-a, 16-43-110350 p-a and the Bilateral Program of the Russian-German Laboratory at BESSY-II.

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# Optical properties of CdTe/ZnTe heterostructures with ultrathin CdTe layers

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Semiconductor heterostructures based on II-VI semiconductors are of great interest due to their promise for applications in electronic and optoelectronic devices. The real properties of these systems depend strongly on the layer thicknesses and the lattice constant mismatches of the heterostructure components. The optical technics make it possible to determine the structure of ultrathin layers embedded in the wide gap matrix.

We have investigated series of CdTe/ZnTe samples containing two ultrathin layers of CdTe of the thicknesses 1.5 monolayers (ML) $L_1$ and 4 ML $L_2$ and different barrier thicknesses. Fig. 1 displays a nominal design of these structures and their photoluminescence (PL) spectra at 5 K.

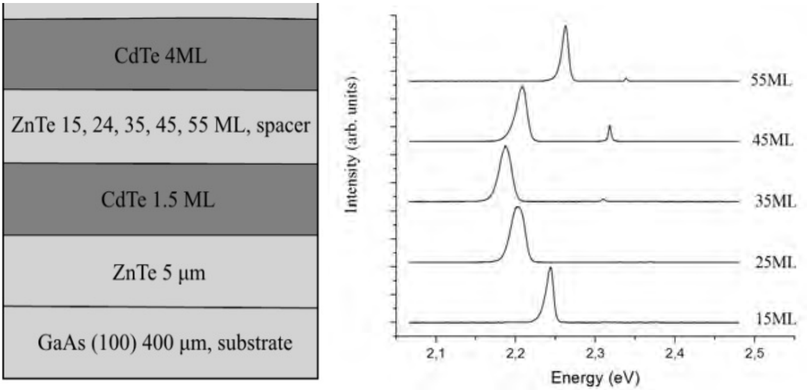

*Fig.1. Nominal design of the samples and their PL spectra. The barrier thicknesses are indicated at right.*

We have studied the temperature dependences of the PL intensities from the $L_2$ layer. In the case of above-barrier excitation, the samples show an increase of PL intensity in the range 5 – 40 K originated from the thermal activation of excitons and free carriers from the $L_1$ layer. The temperature dependences are more complicated under the condition of the below-barrier excitation as a result of the resonance excitation of the $L_1$ layer. The shape of luminescence profiles allows us to conclude that the $L_1$ layer is the uniform ZnCdTe solid solution, while the wider $L_2$ layer consists of plane quantum dots of different lateral dimensions.

# Photoelectron diffraction study of atomic structure of h-BN monolayer on the Co(0001) surface

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Two-dimensional (2D) hexagonal boron nitride (h-BN) attracts considerable attention nowadays due to its remarkable properties, such as large band gap (~6.0 eV), high thermal conductivity, excellent thermal and chemical stability, which determines its significant prospects for applications in 2D integrated electronics and photonics [1].

By means of CVD monolayer of h-BN can be grown on various metal surfaces, among which the cobalt substrate attracts particular attention because of its strong magnetic moment enabling the implementation of spin-valve heterostructures based on the h-BN/Co contacts [2, 3]. The position of the h-BN monolayer with respect to the Co(0001) surface can significantly influence its electronic structure, so high precision determination of the interface geometry represents an important task.

Applying the method of photoelectron diffraction (PED) with the use of multiple electron scattering (MS) calculations allows one to extract quantitative structural information with chemical sensitivity from the angular distribution of the photoelectron intensity. In our work we have used fitting of structural parameters of the model h-BN/Co(0001) cluster to reach maximum similarity of the experimental PED patterns with the simulated ones.

The obtained optimal structural parameters demonstrate that boron atoms preferably occupy hollow sites, while nitrogen atoms are located above Co atoms.

**Acknowledgements.** We acknowledge St. Petersburg State University for research Grant No. 11.65.42.2017.

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# Silicon structures formed on a HOPG substrate by sputtering under ultrahigh vacuum

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Trends in the development of modern nanoelectronics are determined by devices based on silicon. For several decades the main one was aimed at scaling semiconductor devices with increasing performance and reducing power consumption of microcircuits. Within this approach, the development and creation of new nanostructures does not lose its relevance. Calculations based on the density functional theory have shown that silicon atoms can form an ordered two-dimensional hexagonal corrugated structure – silicene – that can have a wide range of applications in nanoelectronics. In addition, silicene can be synthesized and converted using the basic technologies of the semiconductor industry, thereby simplifying the process of integration into existing electronics.

The purpose of this work is to repeat the success in silicone creating on graphite substrates [1] to investigate the properties of the resulting system and also to study how the various deposition conditions affects on the obtained silicon structure. Observations were carried out using an atomic force microscopy, Auger spectroscopy and low energy electron diffraction.

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# Experimental observation of the phase relaxation times of excitons in InGaAs/GaAs quantum well by means of photon echo

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One of the most prospective fields of study in physics nowadays is the nonlinear optics of excitons and their complexes in semiconductor structures, which in the future open up new possibilities for creating optical memory [1]. In this work, the phase relaxation of excitons in a high-quality InGaAs / GaAs quantum well is investigated using photon echo (PE).

The four-wave mixing method (FWM) allows us to explore many effects of the coherent dynamics [2]. Using this method, it is possible to find reversible ($T_2^*$) and irreversible ($T_2$) phase relaxation times. This method uses a two-pulse mode. The first pulse sets the phases of polarizations for an ensemble of excitons, after which divergence begins. The second one, arriving through time $\tau_{12}$, reverses the divergence of the phases. As a result, after a time of $2\tau_{12}$, a coherent pulse from the ensemble is observed, which is essentially a PE (Fig. 1.), and its intensity exponentially decreases with $\tau_{12}$.

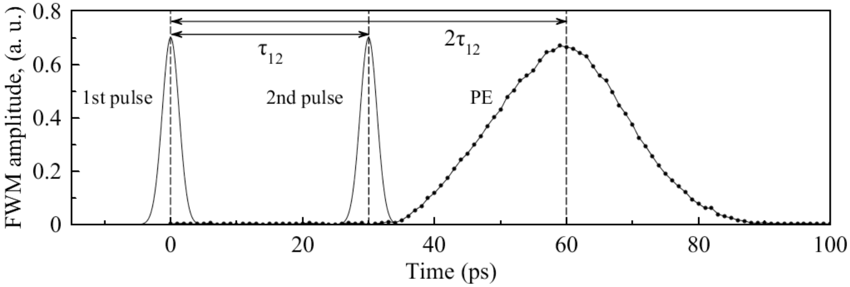

*Fig. 1. Experimental temporal profile of PE.*

It could be explained by the irreversible dephasing of excitons characterized by $T_2$. From the temporal profile of PE $T_2^*$ can be found. The experiment showed that in the InGaAs / GaAs quantum well at a temperature of 1.4 K: $T_2$ = 26 ps, full width of PE pulse is 24 ps. It characterizes the ensemble as homogeneous.

This work was carried out on the equipment of SPBU resource center "Nanophotonics". This work was supported by RFBR grant 16-29-03115 ofi_m.

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# E. Electromagnetic and Acoustical Processes

# Physical effects that occur in a spherical cavity during the interaction of a sound wave with it

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Consider the following problem. In the liquid infinite space, there is a stationary spherical cavity having a radius of the Cavity. In the initial state, the cavity and the liquid medium are in thermodynamic equilibrium. The wave size of the cavity $k_1R<<1$, where $k_1$ is the wave number. With fully interacts flat running sound wave, the parameters of which are known.

It is shown in [1-3] that when a sound wave propagates in a liquid medium, a wave occurs simultaneously with it, which is an acoustic additive to the static temperature of the medium. The interaction of variable temperature with the surface of the spherical cavity leads to the appearance of a non-uniform heat wave in the volume of the gas filling the cavity, which in turn triggers the mechanism of dissipation of acoustic energy. The specific power of the heat flux arising on the surface of the sphere can be found

$$W = 4\pi R^2 q_m$$

where

$$q_m = \sqrt{\chi_2 \beta_{v2} C_{P2}} \cdot \sqrt{\pi f} \cdot T'_{m1}$$

$\chi_2$ – thermal conductivity, $\beta_{v2}$ – coefficient of thermal volumetric expansion of gas, $C_{p2}$ – specific heat of gas at constant pressure.

In the studied physical process another hidden effect. The appearance of an inhomogeneous heat wave in the gas filling the cavity due to the thermoacoustic effect [3] leads to the appearance of a secondary spherical sound wave in it having an amplitude

$$u_{m2} = \sqrt{\pi f \cdot a_2} \cdot \beta_{v2} \cdot T'_{m1}$$

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# Temperature fluctuations in the sound wave

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It is shown in thermodynamics that at adiabatic fluctuations of pressure *P* in gas there is a change of absolute temperature *T* which can be expressed by means of the Poisson's equation, written as

$$\frac{T+T'}{T}=\left(\frac{P+p}{P}\right)^{\frac{\gamma-1}{\gamma}} \tag{1}$$

where *T'* is an acoustic additive to the medium temperature, $p=\rho cu$ is the pressure in the sound wave, $\gamma = C_p/C_v$ is the Poisson's ratio.

In [1-3] it is shown that the acoustic additive to the medium temperature T' changes in time and space synchronously with the vibrational velocity *u*.

To calculate the amplitude of the acoustic additive to the temperature of the medium in the sound wave, the formula can be used

$$T_m' = (\gamma-1)M_a T \tag{2}$$

where $M_a = u_m/c$ is the Mach number acoustic, $u_m$ is the amplitude of the oscillatory velocity in the wave.

Fluctuations in the temperature of the medium lead to periodic fluctuations in its volume. This effect can be taken into account by writing the formula (2) as

$$T_m' = \frac{\gamma-1}{\beta_v}M_a\frac{T}{273.14} \tag{3}$$

where $\beta_V$ is the coefficient of thermal volumetric expansion of the medium. The formulas are applicable for calculating the amplitude in the case when the wave propagates in a liquid. In this case, in these formulas, it is necessary to replace the Poisson's ratio by a nonlinear parameter of the fluid.

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# Amplitude-frequency chaos of self-oscillations in discrete time

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In article [1] as an object of nonlinear dynamics in the discrete time (DT) the discrete oscillator of Van der Pol – Dyuffing is offered (VdP-D). Unlike an analog prototype this DT-oscillator shows the modes of chaotic self-oscillations and can be used as the generator of dynamic chaos. In the present message results of a numerical experiment on a research of characteristics of chaotic fluctuations of amplitude and frequency of self-oscillations are given in VdP–D-oscillator.

The studied self-oscillatory system is set by an algorithm of generation of the DT-signal $x[n]$

$$\begin{gathered} x[n]-2\alpha\cos(2\pi\Omega_0)x[n-1]+\alpha^2 x[n-2]= \\ =\gamma\left(1-\lambda x^2[n-1]\right)\left(\cos(2\pi\Omega_0)x[n-1]-x[n-2]\right)-\mu x^3[n-1], \end{gathered} \tag{1}$$

where $\Omega_0$ and $Q$ – eigen-frequency and quality factor of the linear resonator of system; $\gamma$, $\lambda$ and $\mu$ – parameters of depth of positive feedback, active and reactive nonlinearity.

In space of parameters of the VвP–D oscillator there are areas in which self-oscillations are classified as chaotic. For example, chaos is observed at $\Omega_0 = 0.21$, $Q = 20$, $\gamma = 0.024$, $\lambda = 0.05$ and $\mu = 0.04$. As the mechanism of emergence of dynamic chaos it is offered to consider self-modulation of amplitude and instantaneous frequency of self-oscillations. Are given fragments of temporary dependences of amplitude and instantaneous frequency of self-oscillations.

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# Measurement of magnetic characteristics of magnetic steel

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In order to simulate electromagnetic processes in a drive, it is necessary to know the magnetic properties of materials. Measurements of the properties were carried out using the induction method [1].

During trial measurements, it was noticed that the samples were not demagnetized to the end, so the measurements were made with averaging of signals over two polarities. The initial magnetization curves for all steel grades with small fields lie tightly to each other. For large fields, the curves diverge. Samples of steel 40X differ in size, but they have the same coercive force, residual induction and maximum relative magnetic permeability.

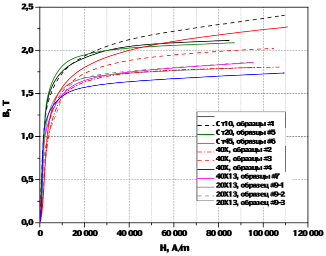

*Fig. 1. Initial magnetization curves.*

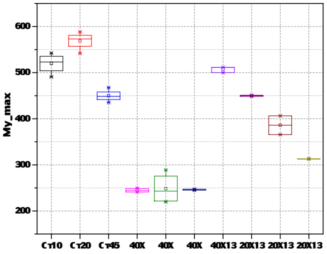

*Fig. 2. Maximum relative magnetic permeability.*

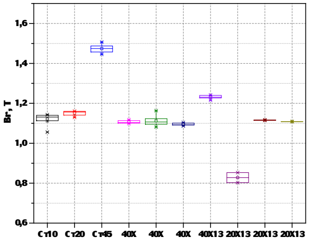

*Fig. 3. Average coercive force.*

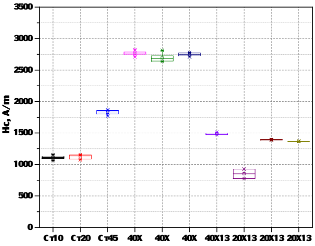

*Fig. 4. Average residual induction.*

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# A simple method to determine the coefficient of interfacial tension for pair "conductive liquid–dielectric liquid"

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The coefficient of interfacial tension (CIT) is one of basic characteristics of a two-phase system. It defines the force, which acts on the interface between two immiscible liquids, the so-called surface tension. The value of CIT is to be known for engineering of various devices such as electric oil dehydrator (where a liquid is suspended in another liquid with differing electric properties) or merging of microscopic amounts of liquids for biochemical analysis, and creating drugs (when the two liquids are situated on a supported surface). Measuring the CIT is a quite difficult task, and very few existing methods have serious disadvantages.

The present work bases on computer simulation of electrodeformation, i.e. the process of changing the shape of a conductive liquid droplet suspended in a non-conductive liquid under the influence of an electric field. The simulation was performed by the finite-element method in COMSOL Multiphysics software package. The equations of electrostatics and hydrodynamics were used, as well as a description of the motion of the interface of two phases.

The dependence of the electrodeformation degree of the droplet on the CIT was described, as well as the dependence on other parameters such as the average value of the electric field, the droplet radius, and the dielectric permittivity. Basing on the comparison of simulation results with available experimental data, the feasibility to determine the CIT value by the electrodeformation degree of the droplet is shown.

The proposed technique of finding CIT has obvious advantages over existing alternative methods.

# Investigation of the effects of anisotropy of ionospheric electron density fluctuations on the coherence properties of the high-frequency wave field propagation in a stochastic transionospheric channel

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This work further extends earlier started investigation into the properties of the mutual spaced position and frequency coherence function of the high-frequency wave fields propagating through the ionosphere with fluctuations of the electron density [1]. The previous work concerning the correlation properties of the stochastic transionospheric signal was limited by consideration of the model case of isotropic random irregularities of the electron density of the ionosphere. However, real random ionospheric irregularities, affected by the Earth's magnetic field, are of essentially anisotropic shape of «ellipsoid of revolution» type oriented along the magnetic field lines, which are additionally placed into the essentially inhomogeneous background ionosphere. This means that the real coherence properties of stochastic high-frequency radio signals propagating through the ionosphere are formed by the mentioned above two effects together. In this work we consider the influence of both the factors mentioned on the coherence properties of the high frequency stochastic fields through the ionosphere.

For the different models of the inhomogeneous background ionosphere the analytic solution of the Markov's parabolic equation for the spaced position and frequency coherence function is constructed. The dependence of correlation properties of this function of the parameters of the background ionosphere and parameters of its anisotropic fluctuations of the electron density, as well as of the geometry of propagation are then studied analytically and numerically for different models of the background ionosphere.

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# Investigation of the properties of plasma jets generated by a magneto-plasma compressor

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Hypersonic aerodynamics is one of the most important fields of applied physics. Theoretical researches and modeling in this field are difficult and expensive. The main advantage of magneto-plasma-compressor (MPC) is simple construction, relative accessibility and high velocity of plasma flow. Which is concerning in this work. The method of estimating ion temperature is analyzing the Doppler broadening of spectral line 424 nm of once-charged nitrogen ion at two points of the plasma jet: the free-flow zone and the stagnation zone near the surface of the aerodynamic model (Fig. 1). According to the experiment, the temperature value is about 2 eV for the free jet and 4–4.5 eV for the stagnation zone, velocity of free jet is above 10 km/s (Mach number), electron density is about $10^{16}$ $cm^{-3}$ (Lines strength).

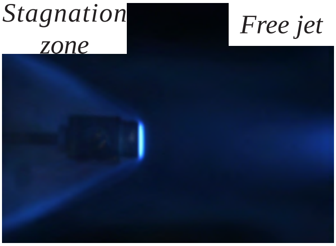

*Fig. 1. Scheme of flow zones*

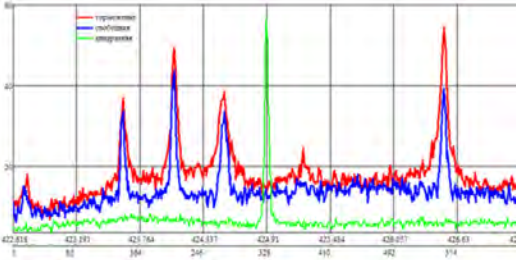

*Fig. 2. Spectral data*

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# Study of the flow of a liquid jet and its splitting into droplets

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A jet of freely flowing liquid, moving under the influence of gravity and surface tension forces, does not remain intact throughout its existence. When falling, the liquid is accelerated, whereby the jet formed by it narrows until at some point it breaks into separate droplets.

Understanding how the jet behaves before splitting into droplets, at what exact moment the splitting occurs and which droplets result from, can be useful for many areas of industry in the development and optimization of various technological processes.

The shape of the jet surface of an ideal incompressible fluid at a potential flat flow without taking into account surface tension is described in [1]. However, a similar approach does not lead to a result in the case of an axisymmetric flow [3].

In this paper, we considered the potential flow of an ideal incompressible fluid, taking into account the action of surface tension forces. A relationship relating the radius of the droplets and the distance between them with the parameters of the jet was derived. A method for the experimental determination of the values involved in this relationship, based on the analysis of the spectral characteristics of the noise of falling drops on a solid surface, is proposed and implemented.

In addition, the shape of the axisymmetric jet is derived taking into account the action of surface tension forces in each of the following approximations:

1) radial velocity component, much less than the velocity component directed along the jet,

2) the effect of gravity is insignificant, which is possible at high velocity and / or a very small jet radius,

3) a case of creeping flow in a very viscous fluid.

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# Computer Simulation of an EHD pump for the flow-type heat exchanger

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Heat removal from microchips is currently one of the most acute problems. The problem can be solved by using electrohydrodynamic (EHD) systems, in which the medium motion arises due to the Coulomb force acting on the charged liquid medium. They have several advantages over other cooling systems. The study aims to design an EHD pump capable of pumping a dielectric fluid without the formation of a charge plug.

The simulation was carried out using COMSOL Multiphysics software. The task calculation based on the Nernst-Planck, Navier-Stokes and Poisson's equations. The radial size of the model is 0.5 mm. A weakly conducting liquid with low-voltage conductivity of $10^{-12}$ S/m was used. The main variable parameter was the length of the pump stage, as well as the change in the number of the latter. The main characteristic of interest is the pumping flow rate.

During the work, various configurations of the EHD pump model were investigated. For each of them, distributions of velocity, charge density, flow rate, and PV characteristics were obtained. For example, in a one-stage model at 10 kV voltage, the flow rate was 0.1 ml/s. However, the configuration with an "infinite" number of stages made it possible to achieve 1 ml/s flow rate.

# Impact of a source size and value of Mach number on some nonlinear effects in a viscous wave field

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We study a finite plate oscillating at frequency **ω** in its plane (along the **y** axis) in incompressible liquid. We showed earlier [1] that the generated transversal viscous waves are nonlinear. We use COMSOL Multiphysics to numerically solve a nonlinear time-dependent set of equations for a 2D problem. It has been found out that finite length **L** of a source causes effects near its edges, i.e. appearance of sign changing pressure **P**, pressure and oscillation velocity gradients; appearance of a longitudinal oscillation velocity component; change of a viscous wave trajectory and some others. The nonlinear effects depend on the source length and its speed **V** of oscillation (an analogue of Mach number $\mathbf{a} = V_y/\omega\delta$, **δ** is boundary layer thickness). The fig. 1 shows pressure and oscillation velocity gradients depending on the plate length relative to **δ** in a moment of time t = 9.25**T** (**T** is a period of oscillation). Finiteness of a source has a considerable effect on values of pressure and oscillation velocity gradient even when **a** is quite small. The dependency is

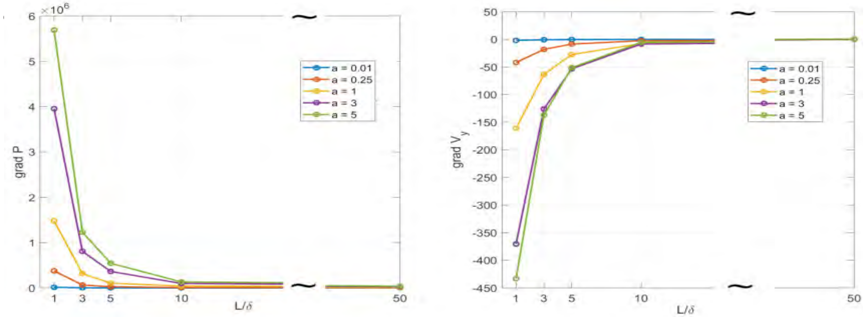

*Fig. 1. Distance to the centre of the source is* x = *0.1***δ***,* y = *0.4***L**

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# UHF and HF conductive and structure properties of magnetic composite films

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Structures of magnetic regions of composite films constituted by ferromagnetic nanoparticles (Co, Fe) in an insulating amorphous a-$SiO_2$, b- $C_2$ and c- $LiNbO_3$ in relation to the metal concentration were investigated in this work. The thickness of the films was 250÷350 nm. The investigated films were received by ion beam sputtering method in the argon atmosphere with pressure 0.04 Pa. The chemical composition of the films and the thickness of the films were determined by the scanning electron microscope JSM-6400. High-frequency (HF) and ultrahigh-frequency (UHF) current loss in the composite films were investigated. Electric circuits of the composite films were proposed to describe the current loss in the composite films. The structures of magnetic regions were obtained by atomic force microscope ARIS-3500.

The HF and UHF current loss in the composite films were obtained by the spectrum analyzer (INSTEK GSP-7830), sweep-frequency generator and element of coaxial cable [1]. The composite films have the varying conductive properties in the high and ultra high ranges of frequencies, which largely are determined by their nano- and microstructures. The complex structures of the films can be represented as a simplified equivalent electric circuits. A equivalent electrical circuit of film was designed. HF and UHF spectrum of the equivalent electrical circuit was obtained. The elecrical parameters of the films is an important characteristic of most materials that are used in electronic devices at high and ultrahigh frequencies.

Work is performed with assistance of the Russian Federal Property Fund (number of a grant: 17-02-01138).

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# Study of the possibilities to increase the efficiency of the flow-type electrohydrodynamic heat exchanger

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The problem of transfer heat in micro and nano-scale thermal control systems is essential for the modern aerospace industry. The smaller and more efficient devices mean higher heat generation. One of the possible solutions is using electrohydrodynamic (EHD) devices, which have several benefits compared to classical cooling systems. The main difference between such appliances from classical ones is that the motion of the liquid arises due to Coulomb force acting on ions, which appear in the volume because of injection and dissociation. The purpose of this study is finding the suitable configuration of the system, which will increase the efficiency of heat transfer.

Comsol Multiphysics software package was used to calculate electrohydrodynamic equations. Several weakly conducting liquids were studied. Various mechanisms of charge formation, such as injection and dissociation were considered.

The results demonstrate that changing properties of the liquid is one of the most successful ways to enhance heat transfer. However, certain configurations of the system show unexpected results, so that further investigations are needed.

# Stationary Harmonic Processes in a System of Two Parallel Cables and a Single Conductor System

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In the course of designing standalone power distribution networks, it is necessary to describe the steady-state harmonic processes of closely-spaced parallel cables systems, as well as single cable systems, bearing in mind that a cable consists of phase conductors, shield and armor. A question of interest is how much and in which cases the standard three-phase description is applicable to these two systems and their various combinations.

Since describing the distribution of electromagnetic fields in high-voltage lines involves matrices of linear parameters (symmetric linear conductance and impedance tensors), a generalized mathematical apparatus for reducing square matrices of order $n$ to $m$ was created to solve the problem, where $m < n$.

The method allows solving the problem of the distribution of current and voltage phasors along a line with varying degrees of reduction. It implies the introduction of a virtual conductor into the system, which contains the elements of lines to be combined. As a result, we obtain simplified matrices of distributed parameters, the dimension of which is reduced by the number of groups of combined conductors or by the number of grounded conductors; this means that we can formulate appropriate conclusions for the above special cases.

The obtained solutions were compared with the results of numerical simulation of the described reduced systems. Ultimately, the differences in the methods turned out to be quite small.

# Formation and properties of the acoustic boundary layer

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The acoustic boundary layer (APS) occurs near the surface of solids when acoustic fields are excited in confined media. According to the works

[1-3] APS is formed in the liquid due to inhomogeneous viscous and thermal waves excited on the surface of the solid. The problems of formation and physical properties of laminar APS arising in the near-wall layer of liquid under the influence of running sound waves are considered in [1, 2]. The conditions for the formation of APS change in the interaction with the flat surface of the body of a standing sound wave, the vector of the vibrational velocity of which is parallel to the surface of the body. This case is considered in article [3], where it is shown that the APS becomes vortex due to the appearance of acoustic Shlichting flows in it.

Vortex APS has the following properties. The thickness of APS $\delta_B$=1.9$\delta$.The amplitudes of viscous waves and thermal waves become dependent on the x-coordinate, and the product $du_m(x)/dx \neq 0$ и $dT'_m(x)/dx \neq 0$.

The density of the heat flux flowing to the surface of the body. The density of the heat flux flowing to the surface of the body $q_2(x)$ also becomes dependent on the coordinate. In the vortex APS, there is an additional mechanism of dissipation of acoustic energy due to the excitation in the wall layer of the vortices of the dressing. The Reynolds number of Shlichting's vortices is always $Re_B \ll 1$, which indicates the effective conversion of the vibrational energy of the sound wave into heat.

In general, when acoustic fields are excited in confined media, both types of APS can exist in the wall layers. Their excitation leads to dissipation of acoustic energy. It can be expected that in the lower part of the sound frequency range these energy dissipation mechanisms are basic.

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# Broadband non-resonant sound source - thermophone

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The emergence of film thermophones allowed on-new to look at thermoacoustic effect and its application in science and technology. The results of experimental studies of film thermophones can be found, for example, in the literature [1-3]. The block diagram of the film thermophone is shown in Fig. 1. The active element (AE) of the thermophone – 1 is applied to the upper surface of the substrate – 2, which in turn is fixed to the upper surface of the carrier plate – 3.

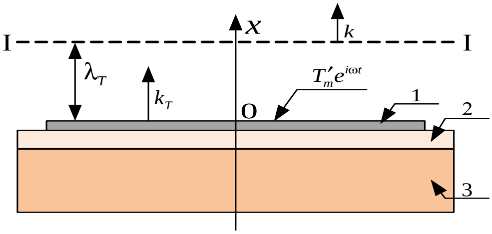

*Fig. 1. Block diagram of the film thermophone: 1-AE; 2-substrate; 3-carrier plate; $\vec{k}_T$ – inhomogeneous heat wave; $\lambda_T$ - the length of the heat wave; $\vec{k}$ – sound wave emitted by the thermophone; I - I - the surface of the sound radiation.*

As a result of the flow of alternating current through the AE with a frequency $f_0$, an alternating temperature occurs on the surface of the AE, changing with a frequency $f = 2f_0$. This in turn leads to the generation of an inhomogeneous heat wave, which, due to the thermoacoustic effect [4], excites a sound wave having an amplitude

$$U_0 = 0,707\sqrt{\omega a}\,\beta_v T'_m$$

where $\beta_V$ is the coefficient of thermal volumetric expansion of the gas.

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# An Electrohydrodynamic Pump Based on the Field-Enhanced Dissociation near Solid Dielectric Surface

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An electrohydrodynamic (EHD) flow is produced by the action of the Coulomb force that sets charged liquid in motion. EHD flow converts the energy of the electric field into the mechanical energy of the fluid. Simple, lightweight EHD pumps having no moving parts and producing no vibration or noise can be more sustainable and effective than usual mechanical pumps.

Recent investigations have shown that EHD flows caused by the field-enhanced dissociation can emerge near solid insulation elements, which makes it possible to create a fundamentally new scheme of an EHD pump, where the key elements of the design are those of solid insulation rather than electrodes [1].

With the help of the software complex Comsol Multiphysics, the distributions of physical quantities in the system «plane electrode – dielectric barrier with a non-symmetrical hole – plane electrode» were computed and analyzed, the pressure-flow rate characteristics of pump were measured.

By changing the shape of the hole, the main characteristics of the pump were optimized. The most preferable system is capable of generating pressure head approximately 2 kPa and rate $1.3 \cdot 10^{-3}$ ml/s, while the size of the main part of the system does not exceed a few millimeters.

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# Investigation of the influence of long-term spatially homogeneous sinusoidal magnetic fields on a drive with a magnetic latch

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The electromagnetic drive [1] is located near the conductor lines. Electric currents with high amplitude values can flow through them. Due to this, there are magnetic fields that can lead to an unplanned disconnection of a closed electromagnetic drive.

Currently, work is underway to investigate the effect of magnetic fields of different configurations on an activated electromagnetic drive. In this work, an experimental study of the influence of a long-term homogeneous magnetic field, which was created by the Helmholtz coil, was performed.

The experiment revealed that an increase in duration of the external influence of the magnetic field nonlinearly reduces the amplitude of magnetic induction, which disconnects the electromagnetic drive and tends to a constant value. The work discovered the dependence of the state of the electromagnetic drive after an external magnetic field on the polarity of the last half-wave of this.

The obtained results can be compared with the finite element model.

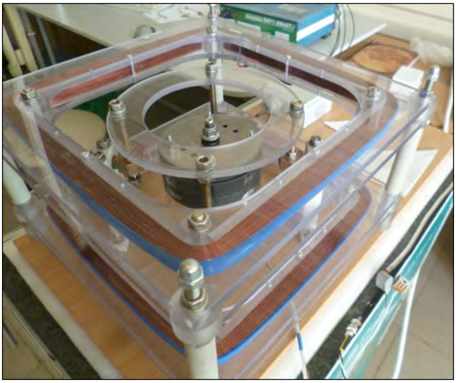

*Fig. 1. Electromagnetic drive placed in a homogeneous magnetic field created by the Helmholtz coil.*

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# Investigation of ion current density in hypersonic plasma flow

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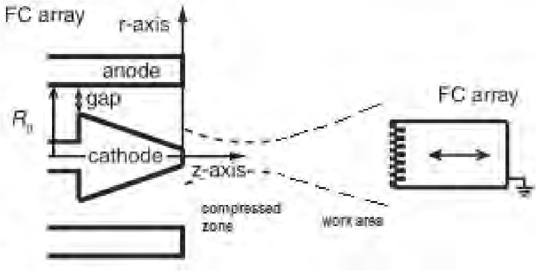
Dense self-confined plasma jet generated by Magneto-Plasma Compressor (MPC) is considered for experimental study of the interaction of bodies with hypersonic gas-plasma jet. The parametres in compressed zone of jet are well known today: range of velocities is amounts 5-10 km/s., stagnation temperature 10-12 eV., $n_e$ – $10^{15}$-$10^{17}$cm$^{-3}$. To use the MPC in experiments, it is necessary to determine the parameters in the work area beyond the compressed zone.

In order to study the spacial dynamics of the flow in aforementioned area the Faraday Cup (FC) array structure was elaborated (similar to FC [1]) to apply as high-ion current sensor. The distance between the cups and geometry of the cups were chosen to prevent electrostatic coupling. The array is grounded to shield the conductors from expected antenna effect. A special sacrificial plate used to ensure the same aperture size for all the measurements.

Knowledge of the parameters of the working area will allow the MPC to be used in experiments to study the interaction of the magnetic field on the shock layer [2] and to assess the effect of plasma on the material of the walls of the TOKAMAK.



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# Optimization of external force influence, caused by a corona discharge, on bulk motion near bluff bodies

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The interest to flow control methods is formidable, as, say, drag reduction can lower fuel consumption. A new way of flow control is electrohydrodynamic systems. However, today, their potential is not realized in full. The presented research suggests efficiency improvement of ion wind impact on drag of a bluff body caused by a positive corona discharge. The proposed suggestion can be applied to other systems, which produce external force in hydrodynamic problems.

The paper studies the influence of ion wind, caused by corona discharge with improved high-voltage wires, on an external fluid flow. There are two types of electrode systems: basic one and improved one, both containing a bluff body – grounded circular cylinder. The basic electrode system also has two circular high-voltage wires, but the improved system has wing-like high-voltage wires. The simulation uses the unipolar model of corona discharge.

It is shown that modified external force significantly changes the wake structure: the drag force changes its sign and starts pushing the body against the flow. In addition, ion wind structures, which usually disappear at strong external bulk motion when basic wires are used, occur in the considered modified system.

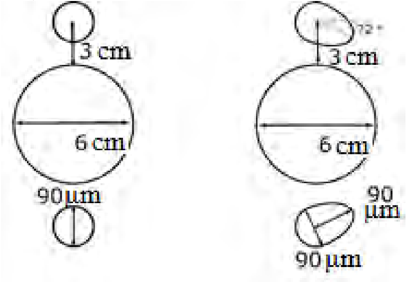

*Fig. 1. The two electrode systems.*

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# Rotational motions of particles in acoustic fields

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The problem of oscillations of a small particle compared to wavelength in liquid under the influence of an acoustic field has been considered many times. It appears in particular in suspensions – liquids containing a lot of microscopic particles. Suspension particles affect propagation of sound altering sound velocity and causing damping of acoustic wave. In general in problem of this kind they consider only influence of particles, whose density and compressibility are not equal to the environment parameters which leads to monopole and dipole oscillations [1]. There are suspensions with neutral buoyancy which means that average density and compressibility of a particle and of surrounding liquid are equal. Such particles do not dissipate sound. However, if center of mass in a particle is shifted, such particle makes rotational motions in an acoustic field [2]. Oscillations are accompanied by viscous friction and lead to energy loss of an acoustic wave. Point weight on the surface of a particle may cause shifting of center of mass. Point weight can be both plus and minus. Minus point weight is a hollow. This effect is studied for particles of different forms, in particular spherical [3] and rod-like particles, and propagation of sound in such suspensions is also analyzed. The solution of the problem of rotational motions of rod-like particles with shifted center of mass in acoustic field has been found. We have derived the formula of energy loss of an acoustic wave in suspension. It shows that the above-mentioned process can lead to considerable damping of wave at high frequencies. We have evaluated coefficient of additional damping of acoustic wave due to viscous loss caused by oscillations.

The following research of the effect under consideration can be useful while interpreting experimental data on propagation of sound in various suspensions. Suspensions of the kind are possible in chemical and technical processes and in biological environments containing microplankton and other microorganisms.

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# The development of the empirical model of the HF radio wave absorption in the ionosphere

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One of the main parameters required for the calculation of the radio channel is the amplitude of the radio wave. That is why it is important to correctly calculate the absorption of radio waves, when reflected from the ionosphere. The purpose of this work is further research of the absorption and development of models, that allows to calculate the absorption intensity of HF waves.

The method, used for developing models, is based on the analysis of ionograms of vertical sounding. It allows to estimate the intensity of absorption at a certain point in time and subsequently create such a model that describes the experimental data as accurately as possible.

Earlier, the empirical formula [1] was studied and modified by introducing the seasonal dependence of the absorption intensity and the coefficient depending on the effective collision frequency. For further development, the same advanced A1 method is used, the essence of which is to compare the minimum observed frequencies of each track of the experimental ionogram and ionogram based on the model [2].

In this paper, it was found that in order to correctly estimate the absorption of short radio waves depending on ultraviolet radiation of the Sun, it is necessary to consider several consecutive days and average the minimum observed frequencies at identical times of days. This averaging reduces the error in further modeling the absorption of short radio waves, and thus improves the accuracy of the developing model.

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# Surface radiation from charge moving along the corrugated structure with a small period

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We consider low-frequency radiation of charge moving along the corrugated conductive surface with a constant velocity which is perpendicular to grooves of the structure. It is assumed that wavelengths under consideration are much more than the period and the depth of corrugation. In this situation the corrugated structure can be replaced with a smooth surface on which the so-called equivalent boundary conditions are set [1]. In fact, we deal with some anisotropic surface characterized by a certain matrix impedance. Note that similar problems were investigated for plane wire structures consisting of thin conductors [2].

In the papers [3, 4] authors examined the problem with charge moving along the symmetry axis of the circular metal corrugated waveguide. It has been shown that the radiation can be generated by the relativistic charge and the radiation intensity is comparable to one in the dielectric waveguide.

Here we investigate the situation when the corrugated structure is planar and has rectangular “cells”. First, we obtain and analyze expressions for Fourier-integrals of components of the total electromagnetic field. It is demonstrated that the ultra-relativistic charge generates the surface radiation, whereas the volume radiation is absent. Besides the field components, we analyze the spectral density of energy losses. Typical dependences of the wave vector and the spectral density of radiation on the geometric parameters of corrugation are obtained.

The results of this investigation are of interest for development of new methods of microwave radiation generation.

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# Physical and numerical modeling of shear wave elasticity imaging

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The study of the Shear Wave Elasticity Imaging (SWEI) method is an urgent issue today, as this method is used actively in the diagnosis of oncological diseases and in the examination of liver disease [1]. With the help of this method, skeletal muscle studies are also being conducted today, which in the future will shed light on many problems of medical bio-mechanics and sports medicine. For this, various models of skeletal muscles are actively created and studied.

In the laboratory "MedLab" of the Radiophysical Faculty of the Lobachesky State University of Nizhny Novgorod, the viscoelastic properties of a phantom imitating a skeletal muscle were studied with the help of the Verasonics research system [2]. It is an universal ultrasound diagnostic device designed to develop and test various algorithms of medical acoustics. The phantom consists of a gelatinous base and elastic strings frozen into it. Based on physical modeling using this phantom and the Verasonics system, it was concluded that the elastic properties of skeletal muscles differ depending on the position of the sensor relative to the fibers, and on the integrity of the matrix from the strings.

Based on the software package k-Wave for the MATLAB environment, the problem of numerical simulation of the SWEI method was solved. There is the possibility of changing the parameters of the environment, which allows one to model a variety of objects under study. The visualization of the results of numerical modeling was realized with the help of Autodesk Maya software.

*Fig. 1. a) Verasonics research system;  b) Virtual model of the phantom.*

This work was financially supported by RSF (Grant No 14-12-00882).

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# Algorithm accuracy used to solve inverse VLF problem during proton precipitation

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In our previous report in Intern. Stud. Conference we have represented the results for solar proton precipitations (SPP) into Earth's ionosphere by the self-consistent (SC) method [1-3] for solving an inverse VLF problem. This report we devote to an error estimation of the corresponding algorithm. The errors analyzed are the following: 1) in the case of time analysis of an event a random measurement error is accumulated from one time point to another; due to this reason the problem of optimal choice of time analysis step appears; 2) a systematic error caused by our usage of a homogeneous waveguide instead of real inhomogeneous one; 3) an error caused by different directions of time analysis as an estimation of SC method.

For the item (1) an optimal step of analysis turn out to be 15 min for the case of proton precipitation 29 September, 1989. Systematic error for the item (2) turn out to be comparable with an apparatus error. That is for the first "ray" ("hop") it is equal to 0.2 microseconds and for the second one – 0.4 microseconds. For the error (3) we have estimated that the uncertainty of effective height determination is equal to 5 - 7 km in the case of maximum disturbances, on 29 September, 1989.

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# Investigation of the amplitude characteristics of signals in the propagation of short waves in the ionosphere

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This study is devoted to numerical modeling of the amplitude characteristics of short radio waves during propagation in the ionosphere. Numerical experiments were conducted to study the formation of an inhomogeneous short-wave structure during propagation in the ionosphere with taking the three-dimensional inhomogeneity, anisotropy, and dispersion of the propagation medium into account. The propagation of both ordinary and extraordinary waves in dependence on a choice of the wave frequency and of geophysical conditions is investigated. To calculate the ray paths and describe the propagation medium, the numerical model of radio wave propagation developed in I. Kant BFU, the experimental models IRI2012 of ionosphere and MSIS86 of neutral atmosphere are used.

The main results of this work are the following:

1. Numerical experiments have been used to study the change in the shape of the radial surface as well as in the cross section while the ray flux propagates in an each of narrow tubes under conditions of ionospheric refraction. As shown, in the region where the tube rotates the local cross section of tube may decrease. This results in the local decrease of attenuation.
2. The formation of a local minimum for the angle between the group and phase velocity of the wave in the vicinity of the turning point of each beam is shown. The expression is obtained for the generalized factor of attenuation of the wave amplitude with taking anisotropy of the propagation medium into account
3. Obtained the conclusion that with increasing frequency the absorption is weakened. During the transition from daytime to nighttime conditions, this contribution falls due to the weakening of decay.

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# Driver Beam Focusing in Rectangular Dielectric Waveguide

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Rectangular waveguides with dielectric filling and vacuum channel are actively investigated in recent years in connection with dielectric wakefield acceleration method. Vavilov-Cerenkov radiation generated by a relativistic electron bunch in a rectangular waveguide is used for acceleration of a small bunch passing through the waveguide. Stability of generating bunch is the main task that is necessary to solve for realization of this acceleration technique. Strict solution of wake fields generated by electron bunch passing through rectangular waveguide with inhomogeneous dielectric filling was obtained in [1-3]. Wake field generated by electron bunch leads to attraction of bunch particles to a waveguide dielectric wall. The idea of bunch stabilization is to add quadrupole structure, to suppress defocusing part of wake field and keep focusing part of it. Thus we obtain focusing on both transverse axes.

We combined solution for the fields generated by the relativistic electron beam propagating in the rectangular dielectric waveguide and added quadrupole-focusing structure. We considered two new methods of focusing: FODO with different section lengths and combination of classical FODO with constant quadrupole and compared them with a focusing by means of reorientation of waveguide sections offered in [4, 5].

On the base of computer modeling it is shown that the combination of classical FODO with constant quadrupole allows to achieve the highest level of energy transformation. The optimal focusing parameters are determined.

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# Interaction of regular and noise intensive acoustic waves

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The interaction of weak noise and regular signals with a shock wave having a finite width is studied in the framework of the Burgers equation model. The temporal realization of the random process located behind the front approaches it at supersonic speed. In the process of moving to the front, the intensity of noise decreases and the correlation time increases. In the central region of the shock front, noise reveals non-trivial behaviour. For large acoustic Reynolds numbers the average intensity can increase and reach a maximum value at a definite distance. The behaviour of statistical characteristics was studied using linearized Burgers equation with variable coefficients reducible to an autonomous equation. This model allows one to take into account not only the finite width of the front, but the attenuation and diverse character of initial profiles and spectra as well [1].

Also the interaction of weak noise with a nonstationary shock front is studied in a medium with a finite viscosity. Owing to competition between amplification at the shock front and high-frequency attenuation, the dependence of the noise intensity on distance has a nonmonotonic character, and at large distances, the intensity tends to zero, while the correlation time tends to a finite value [2].

The work is supported by the grant from the Russian Science Foundation: No. 14-12-00882.

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# Developing the operators formalism for electrodynamics problems in bigyrotropic media

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Bigyrotropic media shows variety of unusual electrodynamic properties, and therefore they are used both by themselves [1,2] and in the complex systems, such as ferromagnetic superlattices [3], waveguides based on magneto-optical layers and photonic crystals [4], thin-film periodic structures of a magnet/semiconductor [5], magnon crystals [6] and so on.

In this study the operator formalism is developed to consider electromagnetic wave processes in stationary, homogeneous, bigyrotropic media. Wave equations are obtained in the general case, and also for waves propagating in parallel and perpendicular to the gyrotropy axis. The solutions of the wave equation and the dispersion relations for the gyroelectric and gyromagnetic waves are analytically obtained. The general method of the solution for waves propagating parallel to the gyrotropy axis is showed.

Developed formalism allows to construct solutions for waves propagating in an arbitrary direction with respect to the gyrotropy axis. In this case the problem reduces to a fourth order partial differential equation. It is also possible to apply this method to the electrodynamics of inhomogeneous media with an arbitrary orientation of the electric and magnetic gyrotropy axes.

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# Delays of the satellite navigation systems signals in a troposphere with horizontal inhomogeneities

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The task of the paper is to determine the phase delays in the propagation of the signal in the troposphere and the effect of horizontal inhomogeneities (gradient) on the delay, using two methods of perturbation theory [1, 2]. Comparison of the results obtained using these methods showed that in most cases the results are close, with the exception of zenith angles greater than 80°. Therefore, in further calculations, an effective spherically symmetric model was used [1]. Comparison of phase delay calculations with simultaneous consideration of the troposphere and ionosphere, and their separate accounting, showed that this difference does not exceed one millimeter for angles less than 80°, and reaches values of about 7 millimeters for an extremely large zenith angle 86° without gradient, and 8 millimeters, with gradient. Thus, separate accounting for the delay in the troposphere and the ionosphere is possible for zenith angles less than 80°.

To take into account the influence of the horizontal gradients of the troposphere, a model of the transition layer described by two parameters was proposed and used in calculations. The parameters are the maximum gradient and the relative refractive index difference on the opposite sides of the area containing gradients. Numerical studies have shown that the influence of horizontal gradients on the phase delay is of the order of tens of centimeters, depending on the parameter values, and at large zenith angles it can reach up to three meters. This is desirable to take into account to ensure higher positioning accuracy.

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# F. Optics and Spectroscopy

# Infrared study of ozone adsorption on zinc oxide

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Zinc oxide is important catalyst and photocatalyst widely used for many applications. However, the attempts to study ozone adsorption on it [1-2] were not successful, despite its high transparency in the IR region. In this work we report the results of low temperature FTIR study of ozone adsorption on ZnO with comparatively high surface area (~60 m$^2$/g).

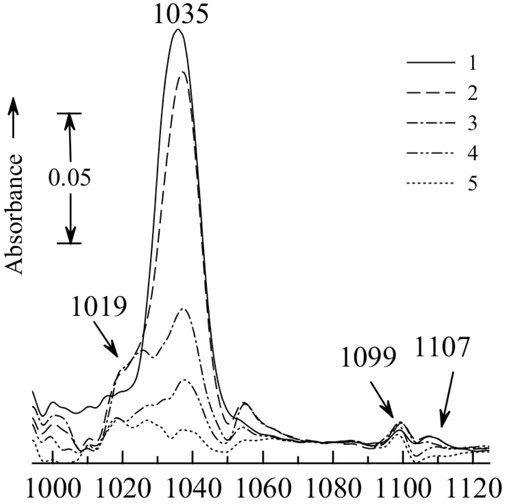

*Fig. 1. FTIR spectra of ozone adsorbed at -196 °C on ZnO pretreated at 450 °C (1), after10 min (2) and at heating the sample up to ~ -160 °C (3-5).*

After ozone admitting into the cell with ZnO sample pre-evacuated at 450 °C (Fig.1) a band at 1035 cm$^{-1}$ arises, typical of weakly bound physisorbed molecules. Its intensity decreases, while a shoulder at 1019 cm$^{-1}$ and new weak band at 1099 cm$^{-1}$ appear several minutes after $O_3$ admission. Meanwhile, the growing pressure in the cell indicates that some ozone decomposition starts already at -196 °C. On heating, the respective intensity of the 1019 cm$^{-1}$ band increases and a satellite band show up at 1024 cm$^{-1}$. As anticipated, the newly found bands of chemisorbed ozone are sifted to lower wavenumbers, as it was found earlier for titania [2].

**Acknowledgements.** The work was supported by RFBR Grant 17-03-01372.

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# FTIR spectroscopic manifestations of niflumic acid aggregation in dissolved, solid and adsorbed state

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Benzoic acid derivatives are widely used in various fields of human activity from food and chemical industry to medicine and the production of LED. Such broad field of applications is due to specific properties of these compounds caused by their ability to form different kinds of aggregates strongly affecting their chemical and photophysical properties. In this work we report the results of FTIR spectroscopic studies of niflumic acid in the solution in $CCl_4$, as supported films or crystalline solid, or adsorbed at the surface of silica or alumina.

The spectrum of the solution is sensitive to the temperature. For the concentration C=$10^{-2}$ mol/l reversible intensity redistribution between the bands of carbonyl groups at 1710 and 1670 $cm^{-1}$ with the isobestic point inbetween enables us to reconstruct the separate spectra of the two structures that account for these bands and can be assigned to monomers and dimers, respectively, (Fig. 1, curves 1 and 2). Spectra of more concentrated solution contain the bands of solid microparticles, the same as in the spectrum of crystalline material pressed with KBr (curve 3). The latter has the C=O band at the position of dimers, but has a very sharp band of C-F groups at 1110 $cm^{-1}$, very sensitive to aggregation due to the resonance dipole-dipole interaction between them.

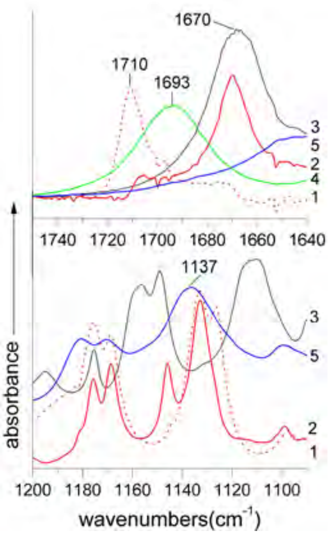

*Fig. 1. FTIR spectra of niflumic acid monomer (1) and dimer (2) in $CCl_4$, pressed with KBr (3) and adsorbed on $SiO_2$ (4) and $Al_2O_3$ (5).*

The spectrum of niflumic acid adsorbed on $SiO_2$ (aerosil) at 110°C (curve 4) has a characteristic absorption band at 1693 $cm^{-1}$, accompanied with silanol band perturbation, thus testifying for monomers forming H-bond with the Si-OH groups. Unlike silica, adsorption on $Al_2O_3$ does not lead to any carbonyl bands above 1650 $cm^{-1}$, but a pair of strong bands at 1590 and 1330 $cm^{-1}$ and a broad C-F band at 1137 $cm^{-1}$ (curve 5). Apparently, the adsorbed molecules dissociate at the surface with the formation of surface carboxylate species.

**Acknowledgements.** The work was supported by RFBR Grant 17-03-01372.

# Physics of localized plasmon resonance on spherical nanoparticles

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The 21st century is the time of the formation and rapid development of nanotechnology. It is difficult to imagine how many benefits it can bring in different areas of human's life.

We study the response of a gold nanoparticle of a spherical shape in the field in optical range.

We used a quasistatic approximation for analytical calculations. Our calculations demonstrate that ideal conductor spherical particles interact with external field as a dipole.

In order to check the coincidence of our assumptions (dipole response of nanoparticle) for real metal nanoparticle, we used fullwave computing by the Comsol MultiPhysics package. We simulate gold nanoparticle field response with a real experimental data for gold electrical permeability using user-equation.

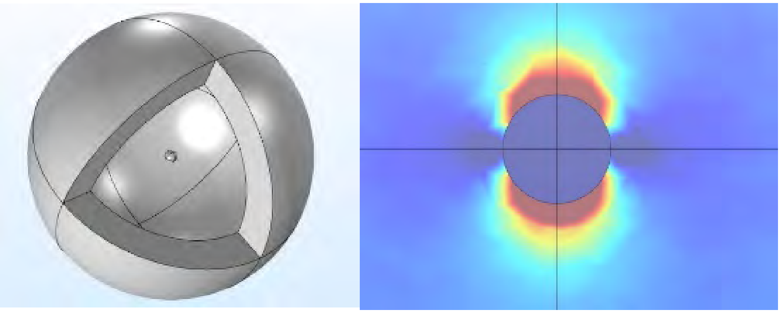

*Fig. 1. a — model with PML for Comsol simulation, b — dipole response of gold nanoparticle*

Simulations shows that the nanoparticle will indeed distort the field as a dipole. In addition, it was found that the size of the nanoparticles affects the value of extinction cross sections. This effect is basic reason of color changes in colloid solutions, stained glass windows and other nanostructured materials.

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# Dark line width measurement in $^{39}$K+$^{87}$Rb cell coated by alkene C30

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Since pioneer work on alkene coated cell investigation [1] there was found the longest (minute) relaxation time in an alkene coated cell with natural mixture of Rb isotopes at very low magnetic field at SERF regime [2]. Only one cell with characteristic size 3cm showed such long relaxation time up to now.

We prepared and investigated 4cm diameter spherical cell with $^{39}$K+$^{87}$Rb cell coated by alkene C30. The cell had lockable stem with the same construction as in [2]. We recorded signals of double radio-optical resonance (DROR) in $^{87}$Rb vapor at stabilized magnetic field B=2000 nT for several pumping light intensities and three radio-field power at each intensity to calculate dark width of the resonance $\Gamma_{0.}$ Fig. 1 shows the smallest recorded signal at T=23$^0$C at the lowest radio-field power and the lowest light intensity. We got at $T_1$ $\Gamma_{0(closed)}$=0.07($^+_-$0.04) Hz, $\Gamma_{0(opened)}$=0.19(±0.04) Hz. At $T_2$ we got $\Gamma_{0(closed)}$=0.4(±0.09) Hz (Fig. 2). Transverse relaxation time was around 2.3, 0.83 and 0.4s respectively. So, we recorded the narrowest DROR signal in such experimental conditions.

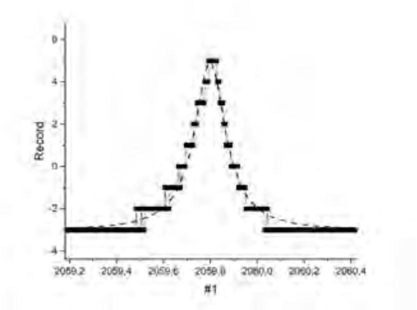

*Fig 1. DROR signal. X-axis units are nT, Y-axis units are arbitrary.*

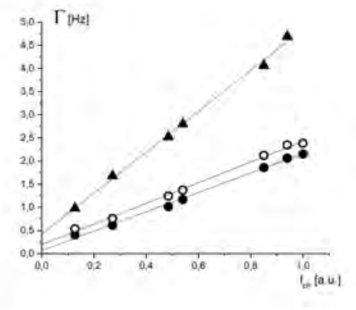

*Fig 2. Conditions:● – T=23$^0$C, stem locked,○ - T=23$^0$C, stem opened, ▲- T=35$^0$C, stem locked.*

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# Optical interference-based sensors for detection of nano-scale objects

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The rapid development of the technologies and nanomaterials leads to the ubiquitous use of nano-scale objects in nearly every industry. Thus, the development of simple, user friendly and cheap devises for rapid detection of nano-objects is a global aim of our project. Taking into account requirement on simplicity of the diagnostic systems the best is to use sensors with optical response due to relatively simple physical phenomenon, ability to measure different properties and to give a legible signal that in some cases can be detected even without special equipment. Towards the achievement of that goal we developed chromogen-free interference-based sensors which provide a color visible reaction directly after interaction of analyte with substrate.

Here we demonstrate, new conception for simple visual detection of nano-scale objects in solutions. We show theoretically and experimentally how interference in thin films can be used as analytical signal for optical sensors. We present the inkjet printing strategy of interference-based sensors with controllable color change. Analytical applicability was approved on the polystyrene nanoparticles with known "nano" parameters and on the Staphylococcus aureus bacteriophage both for qualitative and quantitative analyses (Fig.1). Due to specificity of interference optical analytical signal, two new methods of experimental data interpretation are proposed.

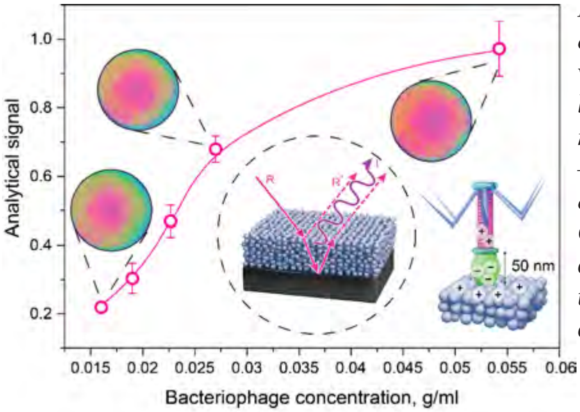

*Fig.1 Schematic illustration of interference in thin films, where R — incident light beam; R* — light beam reflected from interface; I — combination of reflected beams (coloring effect). Calibration curve, average analytical signal as a function of bacteriophage concentration.*

# Optical emission diagnostics of fast phases in development of one-electrode discharge in long tubes

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Recently discovered one-electrode discharge (OED) [1] was observed in long discharge tubes after high-voltage pulses were applied to only one electrode This discharge may have applications in optics and materials processing. OED ignition appears as a multiple travelling of ionization waves (IW) starting at high voltage electrode while the opposite one remains free. IW is the non-linear wave of electric field arising near the active electrode and propagating along the tube and transferring the electrode potential [2]. The report focuses on the experimental study of OED in 1 m long and 1.5 cm Ø tube filled with Ne 1Torr, ignited by voltage pulses with amplitudes ($U_0$) 1.5 – 3.5 kV, rise time 2kV/μs, duration 0.5 ms, repetition rate 5 – 100Hz. Registration of IW optical signals was the single non-disturbed method of plasma investigation. We studied *x-t* diagrams of IW for stable OED for different $U_0$ (Fig.1) and displacement of the plasma boundary in the tube (Fig.2) recording IW optical signals in different tube points.

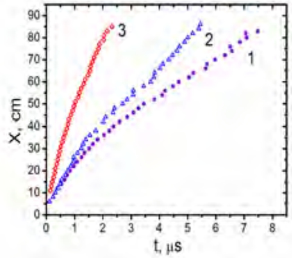

*Fig. 1. Examples of x-t diagrams of IW driven OED $U_0$: (1) 2.1 kV; (2) 2.5 kV; (3) 3.1 kV.*

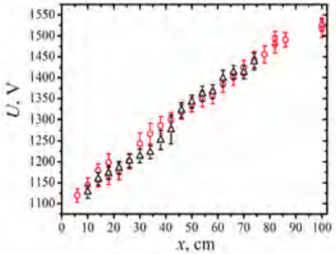

*Fig. 2. Coordinate of OED plasma boundary as a function of voltage amplitude.*

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# Study of the collisional mixing excited Rb-atoms using the method two-photon pumping

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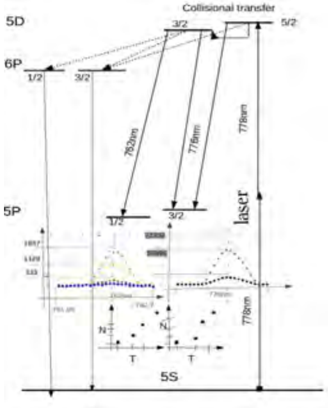
Collisional mixing of excited atomic states connected with optically forbidden transitions($|\Delta L|>1$, $|\Delta S|>0$) is interest because can make a significant contribution to the probability of transitions through intermediate states taken into account in high orders of perturbation theory [1].

The relatively low probability of such processes makes it preferable for studying by the method of selective laser pumping initial levels for transitions without excitation by electron impact in plasma cells. In this work the possibility of experiments like this was tested on the basis of a multi-functional laser resource center at St. Petersburg State University.

Two-photon pumping $5^2D_{5/2}$ Rb-atoms in ground state was made by the *n*arrow-band laser at a wavelength 778nm.The collisional transfer to levels $5^2D_{3/2}$ and $6^2P_{1/2}$ in collisions with ground-state Rb atoms was studying in this work.The reaction rate constants were determined out of dependence the ratio spontaneous fluorescence the final and initial levels in collisional transitions from the concetration particle causing the transition.



As the result of the experiment were got steady signals indicating mixing the states $5^2D_{3/2}$ and $5^2D_{5/2}$. The results to comparison with similar data from [2] and theoretical analysis.

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# Optical thermometers based on $Nd^{3+}$-doped $Y_2O_3$ nanoparticles

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An accurate thermal measurement is in high demand for many areas from technology to biomedical field [1]. Much attention is paid to the development of new classes of non-invasive, non-contact nanothermometers exhibiting superior spatial and temperature resolution as well as high thermal sensitivity [2].

Here, we report $Nd^{3+}$ - doped $Y_2O_3$ nanoparticles synthesized via the combined Pechini-foaming method which are suitable for luminescence thermal sensing in the first and second biological windows. A ratiometric approach, based on the relative changes in the intensities of different emission bands corresponded to the Stark sublevels or excited levels, has been applied to determine local temperature. For each of the selected transitions, the calibration curves were constructed, the relative sensitivity and thermal resolution were calculated. An example of the level scheme and the calibration curve for the transition $^4F_{3/2}$ - $^4I_{9/2}$ is shown in Fig. 1. The obtained results revealed that $Nd^{3+}$-doped $Y_2O_3$ nanoparticles are promising candidates for real biological applications.

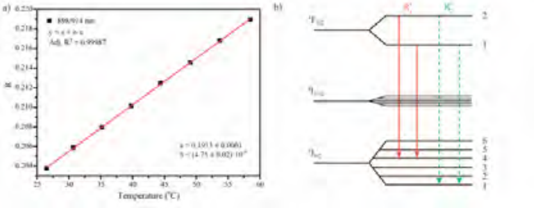

*Fig.1 a) Luminescence intensity ratio as a function of temperature; b) scheme of energy levels transition $^4F_{3/2}$ - $^4I_{9/2}$ for $Nd^{3+}$ ion in the $Y_2O_3$ host.*

**Acknowledgments.** This work was financially supported by Russian Science Foundation (№ 17-72-10055). Experimental investigations were carried out in “Center for Optical and Laser materials research“, “Research Centre for X-ray Diffraction Studies“, “Interdisciplinary Resource Center for Nanotechnology”, and “Innovative Technologies of Composite Nanomaterials“ (St. Petersburg State University).

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# Experimental investigation of materials for anti-relaxation coating by thermogravimetry (TG) and differential scanning calorimetry (DSC)

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Experiments on quantum magnetometry were made with coated cells which contain alkali metal vapor at the cell temperature up to T=100$^0$C [1]. As usually, treatment of experimental results was done under statement when there was no significant evaporation of anti-relaxation coating material at working temperature. Correctness of the statement should be investigated. So, we present results of thermal analysis of two materials for the coating here. First material was a fraction of polyethylene wax (PW), second one was alpha-olefine C30 (Chevron-Phillips). We investigated two samples of each material by TG and DSC. First sample was the material before coating preparation - $1_{\text{before}}$ and $2_{\text{before}}$ respectively, second one was a remains of the material after coating preparation – $1_{\text{after}}$ and $2_{\text{after}}$ respectively. So, we were able to trace the influence of coating preparation procedure on thermal properties of the materials. The investigations were done at Thermogravimetric and Calorimetric Research Centre (SPbGU). Fig. 1 shows the results of DSC analysis, Fig. 2 shows the results of TG analysis.

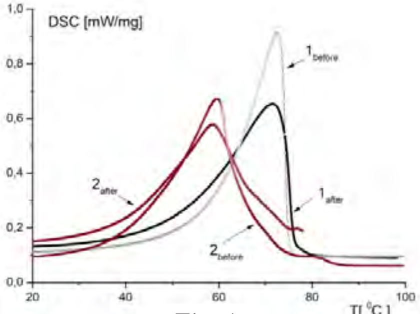

*Fig. 1*

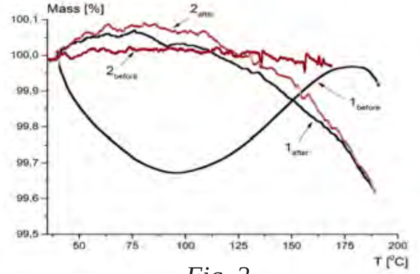

*Fig. 2*

Compare the data for samples after and before coating preparation we see changes in thermal properties of the materials. But, obviously we do not see any significant loss of mass of the samples when the coated cell temperature is less than T=120$^0$C.

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# Inkjet printing of optical waveguides for single-mode opration

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Inkjet printing of high refractive index optical waveguides designed for single-mode operation is presented for the first time. A waveguide core was printed with titanium dioxide nanoparticles that formed a straight strip with a high refractive index. The quartz glass without preliminary processing was used as a substrate. The optimal waveguide thickness to provide single-mode operation in near-IR range was calculated. The number of printed layers necessary to obtain the required thickness and the refractive index was established. The printing parameters to provide suitable morphology for waveguide application were thoroughly studied.

The printed waveguide designed to provide a single-mode regime of operation in the telecom C-band (1.525-1.565 μm) is presented. The importance of the C-band in optical electronics stems from low absorption, material dispersion, Rayleigh scattering in silica optical fibers near 1.55 μm. Another pronounced feature is the availability of high quality optoelectronic components like lasers, amplifiers, modulators etc. often specially designed for the C-band, as well as the eye-safety just to mention. The single-mode regime is of a particular interest in production of PICs because it renders possible to maintain low substrate and cladding thicknesses thanks to high mode field confinement inside the waveguide core.

Measurements confirmed light propagation through the printed waveguides on 1.55 μm wavelength and the mean power loss was estimated as 3.52 dB/cm. The branched structure was printed and its ability to transmit and split light is demonstrated. The received data have a direct applied value for application in future development of integrated optical circuits and printing technologies.

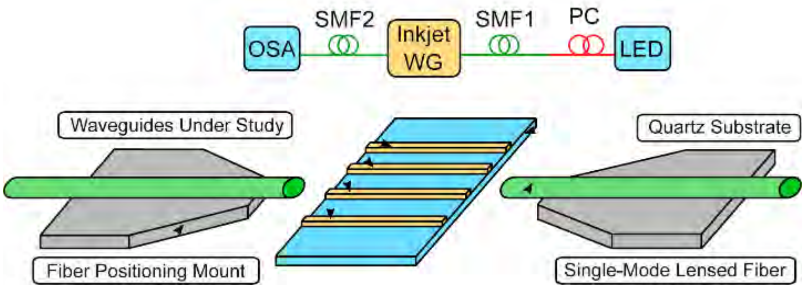

*Fig. 1. Measurement setup and corresponding measurement schema.*

# Modeling of the optical properties of benzene dimer

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The benzene dimer has been widely studied for a long time due to the presence of benzene in numerous biological systems [1]. Benzene is the simplest aromatic hydrocarbon. High dosages of benzene can cause nausea and dizziness, and in some severe cases, benzene poisoning can be fatal. Liquid benzene is quite irritating to the skin. If the human body is exposed prolonged exposure to benzene in small quantities, the effects can also to be very serious, because benzene is a strong carcinogen. That is why instruments that allow to study the concentration of benzene in water are important, and for accurate operation of these instruments data on the optical properties of hydrocarbons are required.

In this work, the absorption spectra of the benzene ring and various configurations of the benzene dimer (Fig. 1) with different distances between molecules were modeled. To check the results, the obtained spectra were compared with experimental data. The results can serve as a basis for continuing work in this direction, including modeling other optical properties of hydrocarbons.

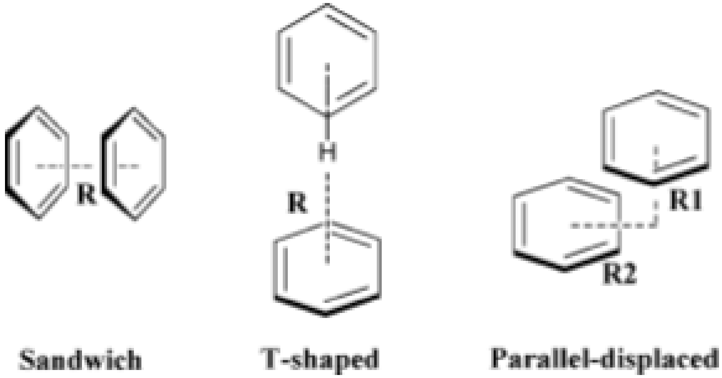

*Fig. 1. Sandwich, T-shaped, and parallel-displaced configurations of the benzene dimer.*

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# Photochemical and photophysical processes in solar cells based on perovskites

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Hybrid organic–inorganic halide perovskite materials have been well-investigated in the past few years. They believed to be very promising candidates for a new generation of printable and efficient optoelectronic devices. These hybrid materials show a good morphology of thin-film coatings, which is very important for conduction in photovoltaics. However, thin-film perovskite layers containing organic cations are highly susceptible to compositional degradation due to both heat and humidity. Therefore, nowadays the replacement of hybrid organic-inorganic perovskites with completely inorganic is the main trend in the development of solar cells [1].

In this study two series of solar cells with different perovskite composition were constructed ($MAPb(Br_{(1-x)}I_x)_3$ and $CsPb(Br_{(1-x)}I_x)_3$). Different electron transport layers were tested as well as different protective layers and electrodes. SEM images of morphology and layers' widths were obtained. The stable operation time was tracked by diffuse reflectance spectroscopy. Some I-V measurements also was performed.

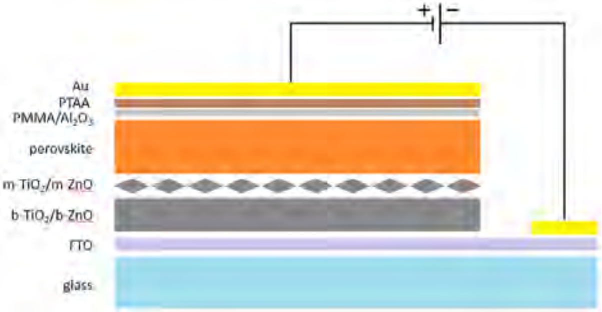

*Fig. 1. General scheme of the constructed single-junction perovskite solar cell.*

**Acknowledgments.** This work was financially supported by a Grant of Russian Government (No. 14.Z50.31.0016) and by Grant of Russian Foundation for Basic Research (17-53-50083 ЯФ_а). Scientific research was performed at the Research Park of St.Petersburg State University «Center for Nanofabrication of Photoactive Materials (Nanophotonics)».

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# Second-order nonlinear effects induced by high-gain parametric down-conversion

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Though the common approach in nonlinear optics is the description of light in a classical way, a lot of interesting effects appear due to its quantum nature. An example is the radiation of spontaneous parametric down conversion (PDC), which is a widely used source of biphotons, squeezed states and other kinds of nonclassical light. In the last years the interest to this field is continuously increasing because nonlinear effects allow one to produce new states of light e.g. three-photon states and to convert frequencies of single photons.

In this research we study the additional second order nonlinear processes that appear due to the high-gain parametric down conversion. Under high intensity of pump laser the spontaneous PDC photons can be amplified that leads to exponential grown of the number of photons of PDC radiation [1]. At the same point the number of photons is large enough that allow one to observe additional nonlinear effects.

In this research the up-conversion and sum frequency generation from high gain PDC [2] are demonstrated. The theoretical description of observed processes is developed. The theoretical description of the up-converted light was developed. The obtained theoretical result explains the observed up-converted spectrum. A completely unexpected result was that the up-conversion is observed without any phase matching though it shows a high efficiency and opens new ways to study PDC.

**Acknowledgements.** This research was supported by G-RISC project P-2018a-16 and RFBR 18-32-00710.

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# Numerical Simulation of Superradiance in a 4-level System

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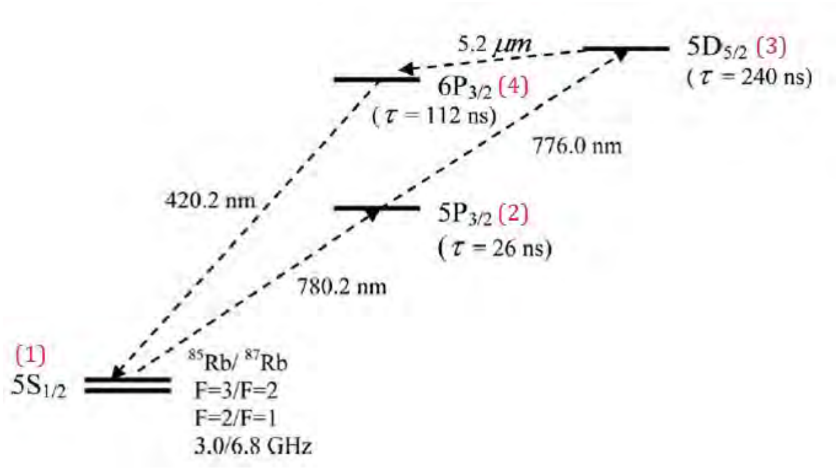

We study the evolution of the ensemble of Rb atoms irradiated by an intence ultra-short laser pulse. The atoms are modeled as 4-level systems shown in the figure. The pulse energy is adjusted to enable the cascade transition to the upper level 3.

In order to describe the relaxation we derive a mean-field non-linear master equation that takes into account the effects of collective interaction of the ensemble with vacuum modes and allows for the description of superradiance.

The equation for the density matrix was solved numerically using the Runge-Kutta method realized in Matlab. The superradience on the transition between the levels 3 and 4 has been observed in the simulations. The dependence of the superradience peak intensity and delay on the atomic density has been investigated. The used approach is general, it can be applied to describe collective effects in different experimental geometries and other relevant conditions.

# Parametrization of optical components drawings with aspherical surfaces

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Expanding the use of aspheric optics leads to the need to accelerate the process of creating these components, including the design process [1]. The necessary method for reducing the time spent at the design stage is to automate the release of design documentation.

Programs that allow to automate the production of optical elements drawings exist, however it do not allow to produce drawings for aspherical optics [2].

The purpose of this paper is to investigate the possibility of automating the release of design documentation for optical elements with aspherical surfaces in accordance with Russian and international ISO standards.

Developed software permits producing drawings of optical elements based on data from such CAE-systems as OPAL PC, SARO and Zemax / OpticStudio.

The report includes:

- the difference in description of aspherical surfaces in CAE-systems;
- peculiarities of execution of design documentation in accordance with Russian and international standards;
- examples of the work of the developed software.

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# Development of the spectroscope training kit for the dispersion phenomena demonstration

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At the Student Research Laboratory for Optical Engineering [1] (Faculty of Applied Optics, ITMO University) students provide educational workshops and develop initiative projects of various complexity levels. For instance, elaboration of laser beam expanders and gaming equipment with reflective elements, design and implementation of "a modular interactive labyrinth" [2], production of optical elements for educational purposes [3] etc.

The aim of the paper is the development of the training kit, which is supposed to be used for the dispersion phenomena demonstration. The paper presents a comparative analysis of various schemes that demonstrate dispersion phenomena and the possibilities of its implementation in the conditions of a student laboratory. The scheme is modeled using CAE system, utilizing the elements available in the laboratory. For the scheme with the best image quality characteristics the design of the training kit is developed. The possibility of manufacturing in the conditions of a student laboratory was taken into account.

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# Surface Enhanced Raman Scattering in the systems with biologically active molecules with azaheterocyclic fragment

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Folic acid (FA) (Vitamin B9) plays a very important role in human organism. Folic acid is involved in metabolism, in the production of DNA, FA plays a significant role in the synthesis of immune blood cells. Therefore, it is very important to control the content of FA in the organism. Surface Enhanced Raman Scattering *(SERS)* spectroscopy was used for the detection of folic acid as one of possible methods for FA detection. SERS is a method widely used to study the properties of molecules adsorbed on metal surfaces. The great value of SERS spectra intensity makes this method as highly sensitive and non-destructive for detection of traces of various substances.

SERS spectra of folic acid adsorbed on the surface of silver electrode and the dependence of these spectra from electrode potential were obtained for the first time. There is no such information on the literature, since the surface of silver colloid particles is usually applied as a SERS-active surface. We observed the reversibility of SERS spectra from the value of the electrode potential. Its dependence from pH of the solution was studied. Optimized geometries of various forms due to keto-enol tautomerism (Fig. 1) of FA molecule in vacuum were obtained by methods of quantum-chemical calculations [1,2].

Calculated spectrum of Raman scattering and IR in vacuum for these forms showed a good agreement with experimental ones. Based on obtained results we proposed the model of adsorption of FA on the surface of silver electrode.

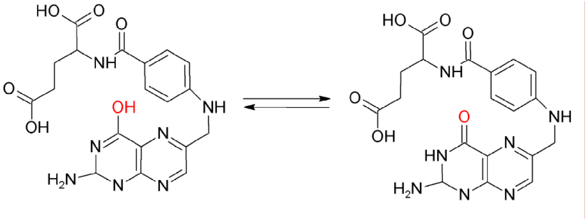

*Fig. 1. Keto-enol tautomerism of folic acid.*

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# Device for positioning mirrors in monitoring layouts

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In various fields of civil and military industry, the most important stage in the designing of any device is the quality control of its characteristics. For optical elements, surface quality plays a special role. Nowadays, new methods of controlling surfaces are being actively developed and more convenient equipment is being developed for control actions. The most common method is interference. In such layouts, control and controlled optical elements are installed in a certain way to obtain a picture that characterizes the surface quality.

The purpose of this work is to create a universal stand for fixing optical elements.

In that work:

- The principles of work of stands-analogues were investigated;
- The construction of the stand for the basing controlled mirrors was offered [1];
- The comparison of the characteristics of the developed stand with analogues was performed.

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# FT-IR spectra of nanoplane graphene and its composition with surfactant

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Graphite nanomodifiers, such as monolayer graphene, are the trend of modern materials science. The introduction of small, no more than a tenth or one hundredth of a percent, additives of carbon nanoparticles with a developed and active surface allows to provide new properties of materials, such as sorption capacity with respect to heavy metals [1], barrier properties, biocidal properties and much more. The main disadvantage of traditional carbon nanoparticles is their high cost, which prevents their widespread use. For this reason, interest in graphene nanoplanes has recently increased, the production of which is based on the physicochemical processes of destruction of natural graphite into separate planes (Fig. 1). The resulting infrared absorption spectra of the original graphite powder and composition graphene nanoplanes with surfactant are shown in (Fig. 2).

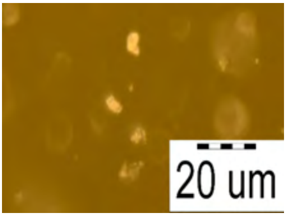

*Fig. 1. Microscopic photograph of graphene nanoplates.*

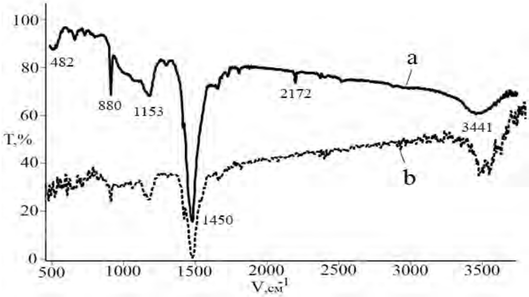

*Fig. 2. FT-IR spectra of composition graphene nanoplanes with surfactant (a) and original graphite powder (b).*

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# Dust particles selection in complex plasma in the dc discharge

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The effect of the particles selection accompanying the self-organization process of complex plasmas in the volume dust structures in glow discharge is investigated. The parameters of the selection of particles: the size and the form-factor are determined. The dependence of selection parameters on type of plasma-forming gas is found. It is established that parameters of selection are linked with levitation conditions (longitudinal and radial forces balances) as well as with the efficiency of particles charging process. The dynamics of the particles selection and the dependence ofselection parameters on the dimensional factor (volume of dust structure) are registered. The found characteristics of complex plasma in the glow discharge are important for understanding the processes of formation of the ordered structures in dissipative nonequilibrium systems.

Work was supported by RSF grant №18-72-10019.

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# Optical properties of epitaxially grown Bragg mirror and quantum well based on GaAs and Al(Ga)As semiconductors

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Microcavity polaritonics is a promising concept for all-optical information processing. The main building blocks of such polaritonic devices are Bragg mirrors and quantum wells (QWs) grown by molecular beam epitaxy (MBE). In this work reflection and photoluminescence spectroscopy were used for obtaining information on optical properties of multilayered structures such as GaAs/AlAs mirror and GaAs/AlGaAs QW.

For instance, normal reflection spectre of Bragg mirror (Fig. 1a) consisting of 10 pairs of GaAs/AlAs layers epitaxially grown on GaAs substrate is well matched with related theory based on method of tranfer matrices defined by Maxwell's boundary conditions. Thicknesses of heterostructure's layers sets the position of the stopband which defined as the highest reflectivity area.

Characteristic photoluminescence spectre of single QW based on $Al_{4.5}Ga_{95.5}As$/GaAs (thickness of the well is 14 nm) grown on GaAs substrate can be seen in Fig. 1b. The main parameter of defining QW quality is the width of photoluminesce peak for it is significally dependent on perfection of a crystal structure. To be exact, for current QW it is small – FWHM = 320 meV (Full Width Half Maximum).

All the gained information on the structures in hand states their high quality as epitaxial structures and could be used futher to set basis for constructing samples such as Bragg microresonators with QW for observing phenomenon of exciton-polariton excitation.

The work was carried out on the equipment of SPBU resource center "Nanophotonics".

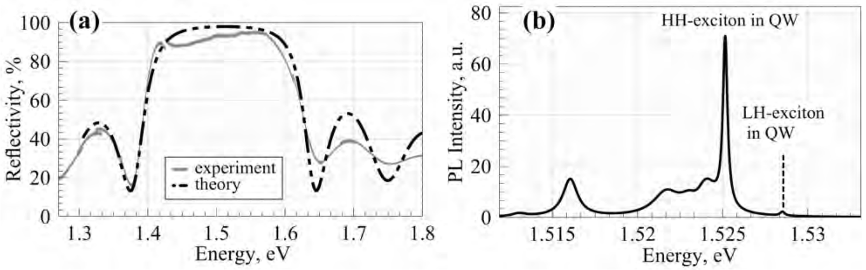

*Fig. 1. (a) - Reflectivity of Bragg mirror; (b) - Photoluminescence spectre of single quantum well.*

# Short-arc Super High Pressure Xenon Discharge Modeling

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Xenon light sources of high and super high pressure, as a rule, have thoriated tungsten cathodes to reduce the work function of electrons. The measurement of the distribution of the emission spectrum along the discharge axis yielded results that cannot be explained without taking into account the evaporation of the material of the cathode (thorium) into the discharge gap. The brightest areas correspond to near-by cathode region where the plasma temperature is much lower than plasma temperature at points closer to the anode. Thorium has a significantly lower ionization potential (6.3 eV) than xenon (12.1 eV) [1], so when it enters the xenon plasma, it easily ionizes and reduces its temperature, while ensuring the necessary degree of ionization for the current to flow.

The aim of this work is to construct a model of short-arc discharge plasma in xenon at high and super high pressure (layers near the electrodes are not included in the review). Modeling is based on the assumptions that the plasma is in local thermodynamic equilibrium and that the radiation in the discharge spot is formed by thorium atoms emitted from the cathode. The discharge structure is well described in elliptic coordinates, where the surfaces $\tau$ coincide with equipotential surfaces (with the surface of the electrodes including), and the surfaces $\sigma$ with the electric field lines. To find the plasma parameters: temperature, electric field strength, concentration of thorium atoms, concentrations of thorium ions and xenon ions, five equations were written: the Saha equations for thorium ions and xenon ions, taking into account the presence of two types of ions in plasma, the power balance equation that takes into account the heating in the electric field and the power loss due to radiation (power losses due to thermal conductivity, as estimates show, are important only near the electrodes), the equation of current through the plasma and the equation of the balance of the number of atoms and ions of thorium.

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# Analysis of ring configurations of confocal resonators

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Nowadays, optical ring resonators have found wide application in various fields. For example, they are used in the laser technology to provide positive feedback, in the gyroscopes as the sensitive elements and as the part of other measuring instruments. At the same time, often in optics the resonators having limited set of eigenfrequencies and equidistant spectrum are required. One of ways of their receiving is the degeneracy of the frequencies of the resonator modes. For example, it is observed in the well-known classical (linear) confocal resonator [1]. At the same time exist similar to him on properties of the configuration of the ring resonators – the ring confocal resonators [2].

This work is devoted to the analysis of various ring configurations of confocal resonators and, in particular, their spectrum.

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# SERS investigation of 4,4'-dimercaptostilbene: optical response and adsorption models on gold nanoparticles

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Electromagnetic interaction of light with the nanoscale gold and silver can generate the collective oscillations of conduction electrons known as the localized surface plasmons. This unique possibility to manipulate with the light-matter interaction at the nanometer scale paved the way for the development of new technological applications of noble metal based materials which span from the surface enhanced optics to plasmon-driven catalysis.

In this work we investigated the adsorption behavior and optical response of 4,4'-dimercaptostilbene (DMS) which served as a modifier of gold nanoparticles. DMS was chosen as the molecule which is able to impart the new functional properties to gold surface. The SERS spectra of DMS were registered in the different range of concentrations and pH as well as at the various compositions of surrounding solution. The study of modified nanoparticles with adsorbed DMS was supported by the UV-vis spectrophotometry and transmission electron microscopy. A chemical state of the DMS molecules on gold surface was also examined by the XPS spectroscopy. In accordance with obtained data the probable adsorption models depending on the experimental conditions were proposed for DMS.

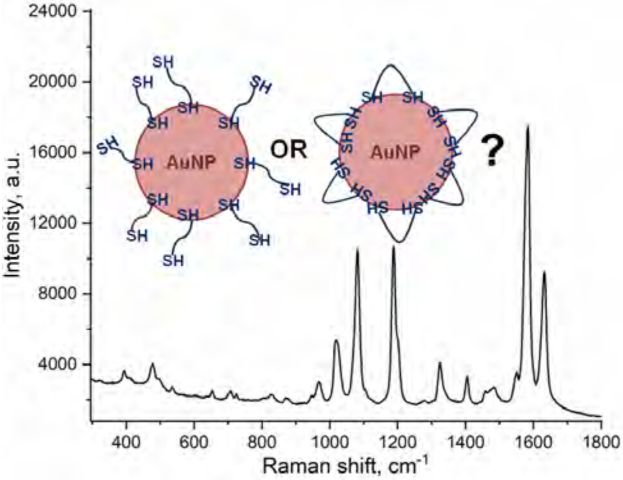

*Fig. 1. SERS spectrum and adsorption models of 4,4'-dimercaptostilbene.*

# Four-atomic van der Waals complexes of iodine in ionpair states

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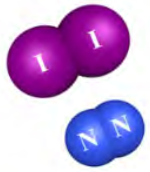
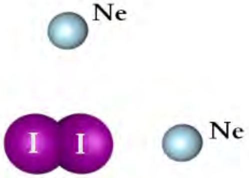
Studies of intermolecular, or non-covalent, interactions play a crucial role for understanding of structure of molecular assemblies, and, consequently, how components of the assemblies interact. Van der Waals (vdW) complexes of halogens with neutral molecules and atoms are promising systems for studies such interactions.

In this presentation, I will report on the $N_2I_2(E0^+_g)$ and $Ne_2I_2(E0^+_g)$ vdW complexes that have been experimentally observed and studied for the first time. These complexes should exhibit different properties, since iodine interacts with a molecular partner in the first case and with two non-interacting rare gas atoms in the second.

Utilization of a standard optical-optical double resonance (OODR) excitation scheme and molecular beam techniques [1] allow us to determine spectroscopic characteristics of the complexes excited states. Binding energies of the $N_2I_2(X0^+_g, v_X=0, n_X=0, B0^+_g, v_B=19, n_B=0, E, v_E=0, n_E=0)$ and $Ne_2I_2(X, v_X=0, n_X=0, B, v_B=19, n_B=0, E, v_E=0, n_E=0)$ as well as some spectroscopic parameters of these complexes have been estimated.

We have also performed *ab initio* calculations for ground states of both complexes. On our assessments, $N_2I_2$ complex has two stable isomers separated with an energy barrier, and $Ne_2I_2$ cluster has four isomers. Possible geometries of the complexes observed in our experiments as well as their decay processes are will be discussed.





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# Characterization of copper species in mordenites by FTIR spectroscopy

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Copper-exchanged zeolites are highly promising catalysts for the removal of nitrogen oxides (de-NOx) and other processes. To improve their properties it is necessary to understand the state of copper sites. Recently it was shown that microwave assisted copper ion-exchange treatment of sodium mordenite leads to diversification of copper species inside the pores [1]. By means of ESR [1] and FTIR spectroscopy [2, 3] one can detect $Cu^{2+}$, $Cu^{+}$ and $[Cu–O–Cu]^{2+}$ species.

The method of isotopic dilution enables us to distinguish bands of single adsorbed molecules from those of binary or triple CO species at the same surface Cu sites. Fig. 1 shows the spectra of CO adsorbed on a sample of Cu mordenite prepared by microwave treatment and evacuated at 450°C. After the addition of $^{12}CO$, three bands arise at 2190, 2161 and 2143 $cm^{-1}$ (Fig. 1a). Evacuation for 10 minutes at 20°C (Fig. 1b), leaves two bands at 2178 and 2146 $cm^{-1}$, while after pumping at 200°C (Fig. 1b) only one maximum remains at 2159 $cm^{-1}$. Adsorption of $^{12}CO$-$^{13}CO$ mixture (30%-70%) results in the appearance of corresponding bands of $^{13}CO$, shifted by *ca* 50 $cm^{-1}$ to lower wavenumbers with respect to the above bands of $^{12}CO$. However the spectrum of the admixed $^{12}CO$ coincides with that of pure $^{12}CO$ only in the case c, while in the spectra a and b the high-frequency bands at 2190 and 2178 $cm^{-1}$ are absent, and single maxima are seen at 2165 and 2168 $cm^{-1}$. This means that it is not the presence of different surface sites, but strong resonance dipole-dipole interaction between two or three molecules adsorbed at the same site that accounts for the complex spectrum of adsorbed CO.

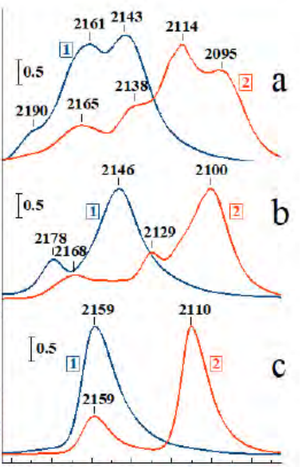

*Fig. 1. FTIR spectra of $^{12}CO$ (1) and $^{12}CO$-$^{13}CO$ mixture (2) adsorbed on Cu-mordenites at progressively decreasing coverages (a-c).*

**Acknowledgement**. The work was supported by the RFBR, grant 18-53-34004.

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# Processes occurring in metal organic frameworks under light irradiation

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Metal organic frameworks (MOFs) appeared to have applications in various fields. Hundreds of papers were published over the past 3 years, where authors report photocatalytical properties of MOFs. One of the most widespreaded tests for photoactive materials is a model test of methylene blue (MB) decomposition over photocatalist. However, there are some issues on using this test in the case of MOFs. To avoid these issues we have developed new procedure to investigate the processes occurs in MOFs during light irradiation.

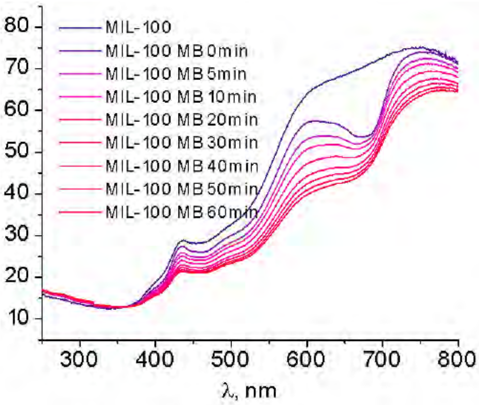

*Fig. 1. SRD spectra of MIL-100/MB irradiated by Xe-lamp (full spectra).*

Our procedure is based on studies of Defuse Reflectance spectra of iron-based metal organic framework with MB. Various charge/energy transfer processes occuring in the system MIL-100(Fe)/MB were found in our experiments. Organic linkers appeared to play the most important role in charge transfer processes. However, it appeared that MIL-100(Fe) does not show any photoactive properties. The processes occurring in the MOF turned up to be more complicated than it was proposed according to the typical test of MB photodegradation. These results were confirmed by other spectroscopic methods.

**Acknowledgements**. The present study was performed within the Project "Establishment of the Laboratory "Photoactive Nanocomposite Materials" No. 14.Z50.31.0016 supported by a Megagrant of the Government of the Russian Federation. The research was carried out using the equipment of the resource centers of the Research Park at the St. Petersburg State University.

# Nonlinear microscopy of organic waveguides

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In recent decades, dielectric microstructures have been actively studied in order to use them in photonic devices. In contrast to inorganic structures, properties of organic structures, such as shape, size and refractive index, are quite easy to manage in a wide range. Among the variety of different shapes of microstructures micro-rods are well-known for their ability to exhibit Fabry-Perot resonator properties as well as waveguiding properties.

In this work, we studied active waveguiding properties of micro-rods made of chiral organic compound R-Binol by the self-assembling method [1], in two-and three-photon nonlinear-optical response using a multiphoton microscopy method. The dependences of two- (2PL) and three-photon (3PL) luminescence intensity on the distance between the excitation and collection points under two circular fundamental beam polarizations were obtained (Fig.1). Measured waveguiding propagation coefficients for the two-photon and three-photon luminescence were 0.14 dB/μm and 0.22 dB/μm, respectively. In addition, the nonlinear optical circular dichroism effect in waveguiding regime was demonstrated with the value of the effect of 10%.

The results can be useful for creating new functional elements for photonic applications, such as microscale waveguides.

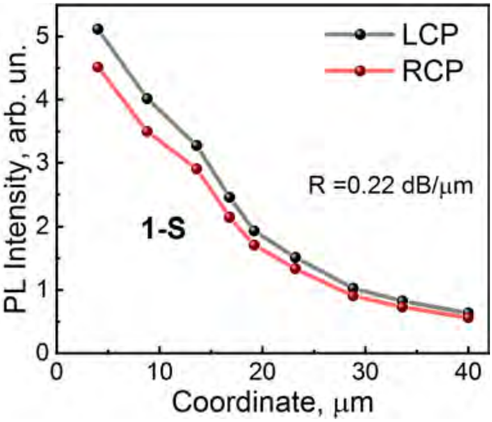

*Fig. 1. Outcoupled 3PL intensity as function of luminescence propagation distance*

**Acknowledgement.** This work is supported by RFBR № 18-32-00710 and RSF № 16-42-02024.

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# Model of signal in Sekiguchi-Hatakeyama experiment with coated cell

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N. Sekiguchi and A. Hatakeyama measured the rate of velocity-changing collisions (VCCs) between alkali atoms and background gas in buffer-free anti-relaxation-coated cells. The background gas was originated from interaction of alkali atoms with freshly-made anti-relaxation coating under vacuum ($P_{residual} = 10^{-4}$ Pa). Alkali atoms were optically pumped by laser D2-resonant light beam with small cross-section. As a result of the process only alkali atom were optically pumped which velocity was almost orthogonal to the beam direction. After that the cell was illuminated by probe pulse of the same laser light, but the beam had much diameter to be absorbed by the pumped atoms which did not changed their velocity due to VCC. So, the experimental result – Sekiguchi-Hatakeyama signal – was dependence of intensity of light of the second pulse passed the cell on time and was sensitive to rate VCC.

The authors of [1] performed calculations using an assumption that Lorentzian spectrum of laser corresponds Lorentzian distribution of atoms velocity projection along the beam $F(v_z,t)$ during the pumping. Further $F(v_z,t)$ tends to Maxwell-Boltzmann distribution due to collisions with residual gas with rate depends to mean free path $\lambda$ through VCC. We calculated $\lambda$ via following fact: the possibility of pumped atom being collided with the gas atom $p(r) = 1-exp(-r/\lambda)$, where r is a distance passed by pumped atom. So we got following plot:

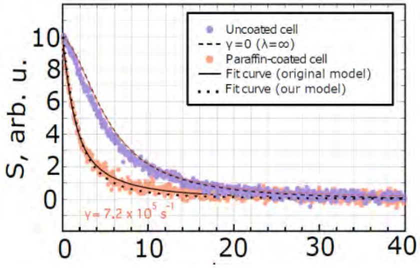

*Fig.1. The signal for cases of coated and uncoated cell. The predictions of both models match up with each other for uncoated cell, but for coated cell do not.*

There is difference between results performed with using different models. Solid black curve is related with original model and corresponds to λ=1.4 mm. Dotted heavy line is associated with our model with λ=0.4mm.

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# Schlieren photography for a visualization process of the vapor stream

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The main task is to register the geometry of the stream of water vapor. To observe the stream, it is proposed to use the schlieren method as a phase-contrast method. The phase contrast method is based on the fact that the refractive indices of individual sections of the structure and the environment are different, as a result of which the light wave passing through the structure of the object changes in phase and acquires a phase relief.

Phase changes of a light wave transmitted through an object using a special optical device are converted into changes in amplitudes, which leads to a weakening or increase in the intensity of light transmitted through the object. The result is an image of the structure of the medium in which the brightness distribution corresponds to the phase distribution [1]. For a more contrasting image, the Schlieren-method is used: a part of the light beam that is not distorted is cut off with a Foucault knife, minimizing excess illumination.

For the experiment, it was necessary to create a reservoir (Fig. 1) where an object for observation (vapor stream) is formed, as well as an optical system for creating a photograph of Schlieren(Fig. 2).

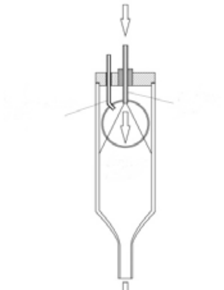

*Fig. 1. Reservoir.*

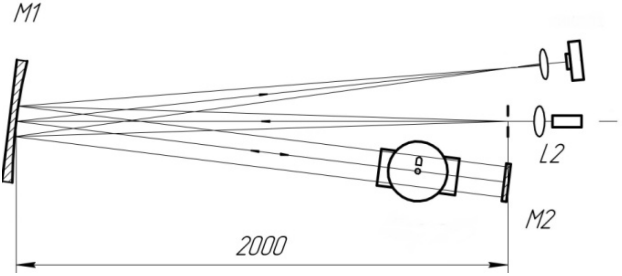

*Fig. 2. Optical system.*

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# Specific features of tomographic applications of spin noise spectroscopy

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Rapid development of nanotechnology devices engineering requires the development of new approaches to spin systems investigations. The method of spin noise spectroscopy (SNS) can be used for nonperturbative studying of the spin dynamics with optical spatial resolution.

The SNS method is based on the Faraday effect. Its basic idea is to observe the fluctuations of the magnetization of the system by measuring the fluctuations of the polarization plane of the light transmitted through the sample in a standard polarimetric scheme.

We fulfilled the experiment that establishes the dependency of total spin noise signal on the beam focus position relative to the probed media. As a model sample, we used a cesium vapor cell.

The goal of this work was to achieve the maximum signal minimizing the optical excitation of the system. It is possible when the Rayleigh length is equal to optical path. In order to maximize resolution one should minimize the Rayleigh length [1]. When the beam is sharply focused on the sample, the volume limited by Rayleigh length and beam cross-section produces the main part of the signal. Thus the saturation of signal power is observed (Fig. 1).

Using the SNS method, we can build a "map" of an inhomogeneous sample, for example, a distribution of GaAs crystal impurities that affect carrier spin dynamics (an example of an experiment is implemented in [2]).

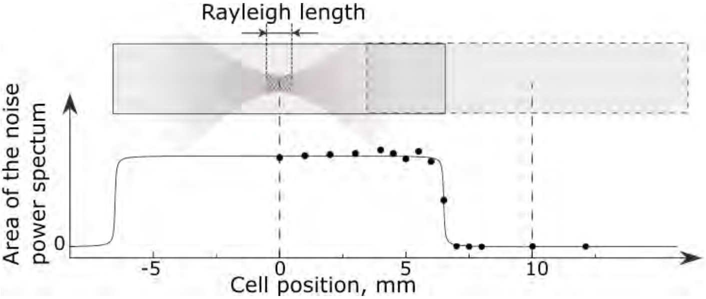

*Fig. 1. Variation of area under the signal curve with displacement of the cell.*

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# Silicon nanostructure fabrication via laser ablation for biomedical imaging

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Silicon nanoparticles are used to diagnose and treat various diseases by means of their high biocompatibility, bioavailability, biodegradability and low level of toxicity [1, 2].

In our work ensembles of nanoparticles formed by ablation of the porous silicon in ethanol and liquid nitrogen exhibit effective photoluminescence (PL) with a peak falling into the diagnostic transparency window for biotissues (with a maximum of 720 nm for laser ablation in ethanol, 740 nm – in liquid nitrogen). Due to the relatively small size (less than 50 nm) of these nanoparticles they are promising to use them as PL markers for imaging of living organisms.

The optical characteristics of the silicon nanoparticle suspensions fabricated by ablation in water and ethanol were studied by spectrophotometry (Fig. 1). It is revealed that the considered suspensions in distilled water and ethanol possess the light scattering coefficients enough to use the silicon nanoparticles as contrast agents in the optical coherence tomography technique.

This work was financially supported by the Russian Foundation for Basic Research (Grant № 18-32-00884 mol_a).

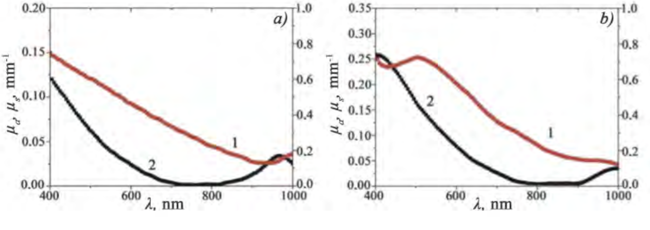

*Fig. 1. The spectra of the scattering $\mu_s$ – 1 and absorption $\mu_a$ – 2 coefficients for samples of porous silicon ablated in distilled water (a) and ethanol (b).*

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# Solubility and phase equilibrium in splitting systems with biofuel components

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Biofuels is one of the leading alternative energy sources. However, it has an inefficient production, which requires an excessive amount of raw materials, for example. Nevertheless, the organization of production can be optimized with the help of scientifically sound methods and taking into account basic thermodynamic and kinetic positions.

The composition of vegetable oils, the main component in the preparation of biodiesel, is rather complicated, so the object of the study is to provide a fundamental model system [1]. As a model, we have chosen the reaction mixture of butanol and acetic acid.

The purpose of this research is the study of solubility and liquid-liquid equilibrium (LLE) in quaternary reacting system acetic acid – n-butanol – butyl acetate – water. The research was conducted at 318,15 K and atmosphere pressure.

The experimental study of solubility was carried out by isothermal titration method. To get the solubility data the special thermostat was constructed. We used the cloud-point technique method to obtain our experimental data. The initial series of quaternary solutions were prepared with the keeping of constant ratio of acetic acid and n- butanol that is 3:1, 2:1, 1:1, 1:2, 1:3. These compositions conveniently display the form of binodal surfaces in composition tetrahedron. The experimental study of LLE was carried out by Gas chromatography method analysis for analytical determination of phase compositions.

Solubility and LLE data were obtained for the quaternary system acetic acid–n-butanol–n-butyl acetate–water at 318.15 K and atmospheric pressure. These set of new experimental data enable to present the binodal surface in composition tetrahedron. Data on solubility and phase equilibrium are well correlated and complement each other.

**Acknowledgements.** Authors acknowledge Resource Center of Saint Petersburg State University "Chemistry Educational Centre". Maria Toikka is grateful for the scholarship of President of Russian Federation (SP-2140.2016.1).

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# Dynamics of the dust structures formed in the double layer in a magnetic field up to 3000G

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Magnetic field is one of the most interesting methods of influence in the study of dusty plasmas, because magnetic field on various components of the plasma impacts on the flow of plasma and on charge of the dust particles.

The potential trap exists in the area of narrowing of current channel formed by placing dielectric insert specially shaped for stabilizing discharge in the discharge tube. In [1] it was found that in this area the dust trap is able to hold a ring shape structure with a large number of particles.

In this work the investigations of the dynamics of the dust structure, which levitating in a glow discharge in a trap in the area of narrowing of the current channel are presented. It has been found that the structure has the shape of a ring with its center coincident with the axis of the hole in the dielectric insert. In the external lonitudinal magnetic field the dust particles are rotating. The value of the angular velocity of each particle is depended on the radius at which the particle is located. Earlier the observations of dust structures in this trap were carried out in magnetic fields up to 400G [2]. In this paper the study in a magnetic field up to 3000 G are presented. The dependence of the angular velocity of the dust structures on the magnetic field is obtained. The value the angular velocity of the dust structures as high as 15 rad/s at the magnetic field of 3000 G.

Finally, we discuss the possible causes of the rotation of the dust particles such as the ion drag force and the effect of dragging by rotating gas owing to Ampere's force [3.4] in a longitudinal magnetic field.

Work was supported by RFBR grant #18-32-00130.

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# Influence of UV-irradiation on the surface properties of $TiO_2$ by the FT-IR spectroscopy

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Titanium dioxide plays an important role in many photocatalytic processes due to its high catalytic activity, high chemical stability, inexpensiveness, and nontoxicity.

In this work we investigated the dependence of the surface properties of $TiO_2$ depending on the degree of its hydration under UV-irradiation in order to understand effect on charge carrier trapping and recombination. Fourier transform infrared spectroscopy (FT-IR) was applied as experimental method. FT-IR method is especially sensitive to water molecules and superficial OH-groups.

Fig. 1 are representing the charge distribution scheme of this material being under UV-radiation. Electrons from the valence band can either be trapped by defect states (shallow traps) with creation of $Ti^{3+}$ species, or in the conduction band. At the same time holes are trapped by oxygen anions forming $O^-$[1]. It was found that UV-illumination of $TiO_2$ surface results in the increase of electrons concentration in the conduction band that manifested by the change of background in IR-spectra.

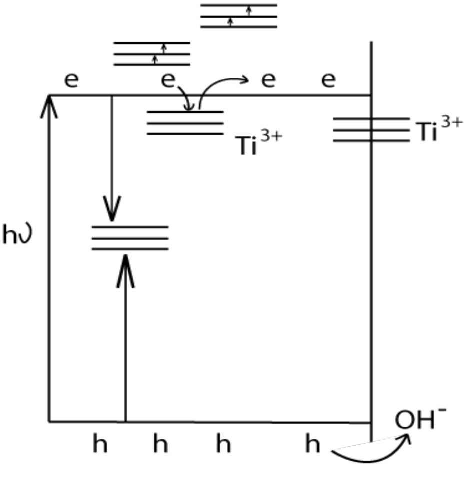

*Fig. 1. Scheme of distribution of charge.*

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# Correlation of spectroscopic parameters of FH···F hydrogen bonds with its energy and geometry

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The idea of hydrogen bond energy estimation from experimentally measurable spectral parameters was first introduced by Badger and Bauer in 1937 [1]. In this work we extend this idea and present correlation dependencies between geometric parameters and energy of hydrogen bonded complexes FH···F with their spectroscopic (NMR and IR parameters). The feature of our approach is that we use local mode model for calculation of vibration frequencies [2].

We considered 26 complexes with FH···F hydrogen bond in a wide energy range. For each complex we calculated complexation energy, IR spectroscopic parameters and NMR parameters.

Based on obtained results we have proposed a number of spectroscopic correlations linking these spectroscopic observables to the complexation energy. The proposed set of correlational dependencies could be used to establish hydrogen bond energy and geometry for other FHF-bonded systems.

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# Features of manufacturing ring confocal resonators

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In the modern world there is a pronounced tendency to downsizing. It extends to navigation. Currently, micromechanical gyroscopes have become widespread. But their sensitivity to accelerations and vibrations limits range of their application. In this regard, relevant research in the direction of minimizing size of overall and precise optical gyroscopes. In most experimental setups and prototypes of miniature (the largest size of sensitive element is from 2 cm to hundreds of microns) of optical gyroscopes, planar passive ring resonators are used [1]. In this case, only single-mode wavewater is used, since the use of multimode waveguides in this case is not possible due to mode dispersion.

For the same reason, most open resonators cannot be used. However, there are confocal configurations of ring resonators with a strongly degenerate and equidistant spectrum [2]. The use of such configurations as sensitive elements allows us to avoid negative influence dispersion of the modes open ring resonator. The use of such resonators instead of waveguides can offer advantages.

This paper is devoted to the analysis of materials suitable for the manufacture of optical confocal ring resonator and advantages of using in compact optical gyroscopes.

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# Spectroscopic study of anharmonic interactions between the overtone 2ν(C=O) and $\nu_1$(HF) bandsin the $(CH_3)_2CO$…HF complex

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Study of the absorption spectra of molecular complexes with a hydrogen bond is one of the urgent problems of modern spectroscopy. One of such complexes with a relatively strong hydrogen bond is the acetone ... HF complex.

It was shown [1], the frequencies of the fundamental transition of the HF oscillation and C=O overtone in the complex can be close, therefore resonance between the modes 2ν(C=O) and $\nu_1$(HF) is possible, so the overtone can borrow the intensity from the mode H-F. Very important and nontrivial task is to determine the contribution of the intensity of the C=O overtone of the free acetone and included to the complex acetone to the shape and the intensity of the observed $\nu_1$(H-F) band. Quantum-mechanical calculations is showed how low-frequency oscillations can affect to the conditions of such resonance [2]. For a more detailed study of this issue we had researched isotope-substituted acetone with $C^{13}$. When $C^{12}$ is replaced by $C^{13}$, the frequency of the C=O stretching vibration decreases by about 2.5% due to an increasing of the reduced mass. So changing of the frequency can violate the resonance $2\nu(C = O)/\nu_1$(H-F) conditions. The infrared spectra of monomers and their mixtures in the gas phase were recorded at the room temperature in the region of 4500-700 $cm^{-1}$ on a Bruker IFS-125HR vacuum Fourier spectrometer with a resolution of 0.05 $cm^{-1}$. The anharmonic potential energy and dipole moment surfaces were computed in the MP2/6-311++G(2d,2p) approximation with BSSE corrections.

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# Ion beam irradiation effect on low-temperature photoluminescence of halide perovskite single crystals

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Recently a lot of investigations have been devoted to the study of halide perovskites due to their properties, which provide the possibility of creating solar cells, lasers and other optoelectornic devices [1]. For the practical application of these materials in photovoltaics, optoelectronics or informational photonics, the technology of manufacturing nanostructures using ion beam etching may be useful.

In this work effect on irradiation of 30 keV with $Ga^+$ ions on $MAPbBr_3$ ($MA = CH_3NH_3$) single crystals was studied. Sample was irradiated with doses of $10^{11}$-$10^{17}$ $cm^{-2}$. For the model of exponential extinction of the luminescence from the dose, characteristic doses were obtained. Exciton luminescence has characteristic doses in order of $10^{14}$ $cm^{-2}$, which is two orders of magnitude more than the characteristic dose for integral luminescence ($10^{16}$ $cm^{-2}$).

This work was carried out by the equipment of SPBU resource center "Nanophotonics".

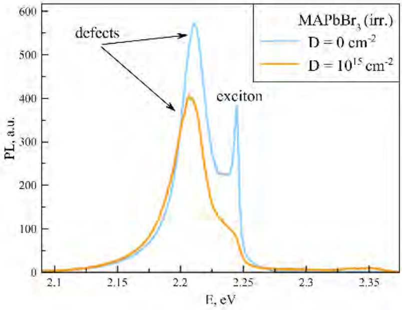

*Fig. 1. Photoluminescence spectra of irradiated (D=$10^{15}$ $cm^{-2}$) surface and unirradiated.*

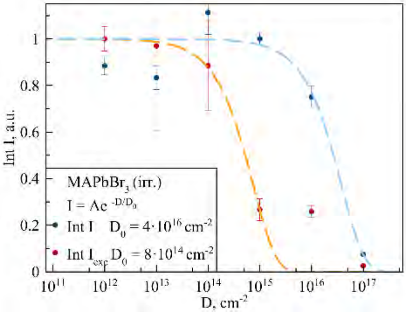

*Fig. 2. Dependence of photoluminescence $MAPbBr_3$ single crystals from the dose of 30 keV $Ga^+$ ions.*

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# Matrix isolation of phosphinic acid complexes

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The method of matrix isolation consists in placing individual molecules or groups of molecules in a cell of a matrix consisting of an inactive substance that practically does not interact with the object under study. In addition to the fact that the spectrum of molecules is recorded at low temperatures, using this method it is possible to prevent the interaction of particles of the object being studied with each other and to eliminate the influence of foreign objects on the molecule. On the other hand, the molecules are not in the crystalline phase. Thus, almost all molecules are in the ground state, and, as a result, the spectrum under study becomes very simple. This method allows one to study not only individual molecules and their various configurations in the matrix environment.

The method is well suited for the main task of this work: the registration and analysis of the absorption spectra of phosphinic acid and the complex with the participation of its molecules, placed in a matrix of matrix gas. In the course of the present work, the absorption spectra of dimethylphosphinic acid and its mixture with perdeuterated fluoromethane in argon and nitrogen matrices were obtained. The setup used in the experiment allows an annealing procedure to be performed on the matrix, after which the matrix objects are redistributed to a more favorable energy configuration (Fig. 1).

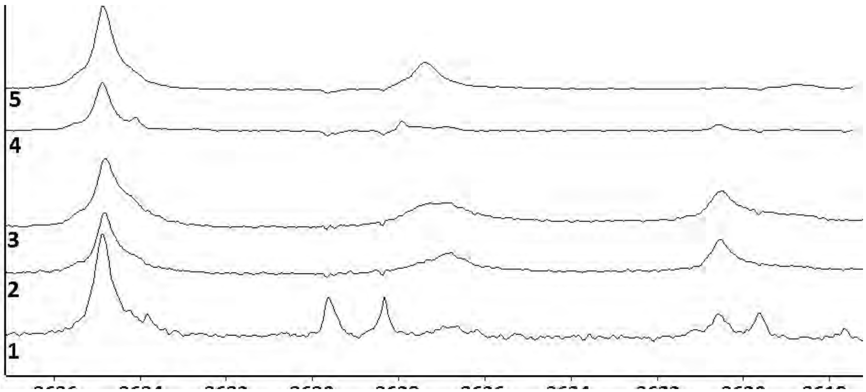

*Fig. 1. Spectra obtained: 1 – $CD_3F$; 2 – (CH3)2POOH + $CD_3F$ aft. ann.; 3 – (CH3)2POOH + $CD_3F$ bef. ann.; 4 – (CH3)2POOH aft. ann.; 5 – (CH3)2POOH bef. ann.*

# G. Theoretical, Mathematical and Computational Physics

# Development of a component of HTML5 dynamic graphics for virtual physics laboratories

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During the last decade the collaboration of Saint-Petersburg State University and IFMO develop worldwide unique server-client assessment system with virtual laboratories in physics [1]. The system is designed to provide users with an opportunity to carry out computer-aided assessment in physical experiment with a high level efficiency. It is possible to emulate various experiments with server generated parameters [2]. This system finds practical use in Saint-Petersburg State University and IFMO for online competitions (Olympiads) of schoolchildren.

Today the system uses models which are written on BARSIC programming language [3] – domain specific language. These models work on Windows and Linux platforms only. One of today's main aims is making labs cross-platform. Despite the fact it is still possible to maintain a set of programs for Android, Windows, IOS, etc., instead of one, it turned out that there is a better idea: using HTML 5/ JavaScript opportunities with Java (or Swift and so on) shell. This approach seems to be more efficient according to:

1) Unified graphical interface – it is important to show user the same picture on every device.

2) Unified painting rules – different operating system platforms can interpret the same code in different fashions.

3) Acceptable speed – HTML 5/JavaScript code will be interpreted by high efficient multiplatform browser component, such as Webview.

4) Security – HTML 5/JavaScript code itself is not protected from viewing, however Java (or Swift and so on) shell do these code secure.

Prototype of the system is developed with Java shell for Android platform.

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# On the Baxter’s Q-operator for the quantum nonlinear Schrodinger equation

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Baxter’s Q-operator is an effective tool for studying quantum integrable systems, though no regular method of its constructing exists so far. A. A. Tsvetkov showed [1] that integrability of some known systems follows from commutativity of one family of operators. In this talk we show that in the case of nonlinear Schrodinger equation Tsvetkov’s operator is exactly Baxter’s Q-operator for this model. We propose a simple method for deriving its properties and discuss its relation to quantum inverse scattering method.

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# About predicting oil production by the characteristics of water displacement

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One of the approaches to predicting oil well production is based on an analysis of the dynamics of the yield of liquid (oil + water) for the previous period. The dynamics of oil well production is calculated based on a given dynamics of the liquid yield and the watering characteristic, which determines the dependence of the water cut on the degree of production of recoverable reserves. The input data for this considered method are actual oil data of total oil wells production, the dynamics of liquid yield for every wells, the volume of initial recoverable reserves (IRR) for wells. The water cut as a function of the production of initial recoverable reserves is well described by the parametric correlation model Corey [1]. For its construction in the case of a specific well, the calculation of three parameters from production data is required.

In the present work, the problem of estimating the minimum amount of initial data sufficient to build an acceptable predictive characteristic is solved. The proposed algorithm is implemented on the basis of the simplest neural network with one hidden layer [2]. The network was trained by the backpropagation method, in which studying the effectiveness of training schemes with different numbers of input parameters in order to obtain the best prediction for the minimum initial data set.

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# Determinant representations for the partition function of the five-vertex model

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The five-vertex model is a special case of a the six-vertex model in which one of the vertices is frozen out. This model describes non-equilibrium processes [1], and it is also related to the problems of enumerative combinatorics. Configurations of the five-vertex model are in one to one correspondence with weighted plane partitions (three-dimensional Young diagrams) [2].

In this work we consider the five-vertex model on a (2N + K) x M lattice with fixed boundary conditions. Namely, the external horizontal edges of the left and right boundaries are all empty, on the top boundary the first N vertical edges are empty and the remaining have lines on them, on the bottom boundary the first (N + K) vertical edges have lines and the remaining are empty. The boundary conditions of this specific type make it possible to use the Bethe Ansatz technique for calculation of the partition function. This method is famous for its effectiveness in the studies of vertex models, particularly for the five-vertex model wave functions were represented as determinants which are up to normalization factors given by Grothendieck polynomials [3].

Our main result is generalization of [4], where the five-vertex model on a 2N x M lattice was studied, to (2N + K) x M lattice. In terms of the plane partitions this means changing the size of the box from N x N x (N – M) to N x (N + K) x (N – M). We obtain two determinant representations for the partition function: as determinant of the matrix with the size of (2N + K) x (2N + K) which is equal to number of operators in corresponding scalar product and as determinant of the N x N Hankel matrix. We obtain closed form for the homogeneous limit of the determinant as well.

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# Molecular dynamics simulations of conducting polymer blend PEDOT:PSS

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Organic conducting polymers have been used in bioelectronics engineering due to their biocompatibility and flexibility during processing [1]. Because conducting polymers support the transport of both electrons and ions [2], in contrast to conventional semiconducting materials, they are used in a variety of biomedical applications [3]. Among all conducting polymers the poly(3,4-ethylenedioxythiophene) (PEDOT) and its derivatives are the most used ones in bioelectronics [4]. High conductivity of PEDOT is achieved in a doped state (PEDOT:PSS) where positive charges in the polymer backbone are compensated by negative polymeric counterions (polystyrenesulfonate – PSS). Despite many experimental findings [5, 6, 7], there are difficulties to obtain experimental data about the microstructure of the conducting polymer blend, due to the disordered and nano-crystalline morphology. Molecular dynamics simulations could therefore provide access to structural models of such polymer mixture [8].

In this work we report the results obtained by the computer simulation of PEDOT:PSS aqueous solution.

*Fig. 1. Representation of dimer unit of PEDOT and monomer unit of PSS.*

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# Electromagnetic instability in strongly magnetized plasma in the presence of a neutrino flow

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The problem of explosions of supernovae of 2nd type is still not fully solved problem in modern astrophysics. It's known that in early numerical simulations explosion did not occur: stalled shock wave falling backward to core of dying star [1]. One of the possible solutions of this problem is finding the source of heating of shock wave. It is neutrinos, flowing through the stalled shock wave and producing electromagnetic instability that could revive it. This process is similar to the well-known electron beam plasma instability. But it was shown that in the absence of external fields in shock wave, the effect from the realization of such an instability is extremely small [2]. However, there are several mechanisms for the generation of rather strong magnetic fields in the shock wave region [3]. In addition, it is known that in the presence of strong magnetic fields, neutrino-photon processes could be catalyzed. [4]. Therefore, it is interesting to study the electromagnetic instability in a strongly magnetized plasma in the presence of a neutrino flow.

In our work, the photon polarization operator in a strongly magnetized electron-positron plasma in the presence of a neutrino flow is calculated. Two different regimes of instability, hydrodynamic and kinetic, are analyzed. It is found that in the hydrodynamic regime the expression for instability increment contains square root singularity in the vicinity of the electron-positron pair creation threshold. As a consequence, this fact could lead to a significant increase in the energy transfer from the neutrino flow to the shock wave. Numerical estimations of the dependence of the instability increment on the plasma temperature are obtained.

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# Extension of the analytical calculation of the fast relaxation spectrum in micellar solutions

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Relaxation processes to the state of aggregative equilibrium of micellar surfactant systems are described by the Becker-Dering kinetic equations for aggregate concentrations. The finding of the spectrum of the relaxation times with the help of these equations is possible only numerically and requires a large amount of computer calculations. Analytical calculations are carried out by passing from the system of difference Becker-Dering equations to differential equations in which the number of molecules in a micelle is considered as a continuous variable. In combination with the parabolic approximation of the micelle formation work, this allows one to find analytical expressions for the spectrum of relaxation times [2]. The comparison shows that there are both quantitative and qualitative differences of this spectrum from the numerically calculated one. In particular, the presence of degeneracy, which is absent in the results of numerical calculations, takes place. In [3] corrections to analytical eigenvalues were found with the help of perturbation theory. This improves the agreement with the numerical values and removes the degeneracy of the spectrum. However, the approach used in [3] reveals the drawbacks associated with the non-self-adjointness of the perturbation operator, which in some cases leads to unphysical complex values of the relaxation times. I propose a modified version of perturbation theory in which the self-adjointness of the perturbation operator is preserved in any order of perturbation theory, which guarantees the reality of the relaxation times.

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# The generalization of the equations of motion of the splitting theory

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We investigate the splitting theory [1], which is one of the field theoretic formulations of gravity. This theory describes gravity as a field theory in a flat bulk of higher dimensions. It deals with N-4 real fields $z^A$ in N-dimensional Minkowski space with the Lorentzian coordinates $y^a$. Each field configuration $z^A$=const corresponds to some splitting of a bulk into a system of 4D surfaces. Any surface can be considered as our spacetime.

The action of the splitting theory can be constructed as the sum of the Einstein-Hilbert actions of each surface over all the surfaces and finally can be written as

$$S=\int dy\sqrt{w}R$$

This action gives the Regge-Teitelboim equations [2] in the field theoretic form:

$$b^{a,}_{cd}G^{cd}=0,$$

where $b^{a,}_{cd}$ is the second fundamental form of the surface and $G^{cd}$ is the Einstein tensor.

It should be noticed that the splitting theory possesses the symmetry under "the renumeration of the surfaces"

$$\tilde{z}^A(y)=f^A(z^B(y)),$$

where $f^A(z)$ are arbitrary functions. This symmetry shows that the physics depends only on how we perform the splitting of a bulk into a system of surfaces, but not on the actual values of fields $z^A(y)$ on each surface. The action of the splitting theory is not invariant under "the renumeration of the surfaces", because of $\sqrt{w}$, but the equations of motion are invariant.

We generalize the action of the splitting theory in the following form

$$S=\int dy\varphi(w)R,$$

where $\varphi(w)$ is an arbitrary function. We analyze the corresponding equations of motion and choices of $\varphi(w)$ (apart from $\varphi(w)=\sqrt{w}$), for which these equations of motion stay invariant under "the renumeration of the surfaces".

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# Bremsstrahlung radiation from twisted electrons

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Photon is called twisted (or vortex) if it carries the non-zero projection of an orbital angular momentum onto its propagation direction. Due to the non-zero value of this projection, the twisted photons have found extensive applications. This in turn requires the twisted light generation over the broad range of energies. Meanwhile the techniques of the twisted photons generation in the optical and XUV ranges are presently well established, the creation of the vortex x-rays is more involved. To the best of our knowledge, no twisted photons with energies greater than 9 keV have been produced so far. In the framework of the present project, the possibility to generate vortex x- and gamma-rays using bremsstrahlung from high-energy electron scattering from an atom is considered.

Two different scenarios will be studied. In the first one, the incident electron is assumed conventional (plane-wave) and twisted in the second one. For both scenarios, the “twistedness” of the bremsstrahlung will be evaluated. Additionally, the accurate theoretical analysis of the bremsstrahlung from twisted electrons scattering from atoms will be performed. We compare the results we obtained in the first scenario with the results of Yerokhin *et al.* [1].

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# Application of the two-dimensional time formalism to the magnus expansion

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Laser-matter interactions produce very interesting effects that can be examined experimentally due to recent success in building ultrashort intense lasers. However, a theoretical description of the phenomenon is also a subject of interest. Researchers have developed and used a number of techniques that solve the problem. Among them the Magnus expansion was helpful in computing the time evolution operator (TEO) for the hydrogen atom in the few-cycle laser pulses of particular types [1]. At the same time, the two-dimensional time formalism [2] played an essential role in studying carrier-envelope phase (CEP) effects [3].

In this paper we aim at examining an application of the 2D time method to the impulse approximation, which is the first term of the Magnus expansion, for solving the time-dependent Shrodinger equation for a two-level system in a laser field.

We numerically compare the combined approach with the ones standing alone, finding regimes in which the technique gives satisfactory results.

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# Neural networks based methods for solving the equations of quantum mechanics: developing the cost function

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We propose and investigate a new approach to constructing the cost function for solving the equations of quantum mechanics. Our approach is based on training the artificial neural network (ANN) to represent an invariant subspace of the Hamiltonian. The network is then used as a basis for solving the Schroedinger equation. The one-dimensional quantum harmonic oscillator is used as a benchmark problem. The Nelder-Mead and the differential evolution methods are used for optimization.

The following function is proposed

$$J(\vec{w},\vec{x}) = \frac{1}{m}\sum_{i=1}^{m}\left(\sum_{j=1}^{M}\hat{H}N_j(\vec{w},x_i) - \sum_{j=1}^{M}\alpha_j N_j(\vec{w},x_i)\right)^2 + G(\vec{w},\vec{x}) + L(\vec{w},\vec{x})$$

Here $H$ is the Hamiltonian, $N$ is the neural network, $w$ is the set of weights, $m$ is the number of collocation points, $M$ is the number of ANN outputs, and $\alpha$ is the set of linear regression coefficients for approximation of the net images by the net outputs. The term $G$ governs the boundary conditions, and $L$ ensures the linear independence of the ANN outputs.

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# Insights to ESR spectra from molecular dynamics simulation

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In general, investigation of a spin system evolution with a stochastic Hamiltonian requires knowledge of dynamical statistics to obtain observables. Usually those statistics are not known and their characteristics are a subject of speculation. The differences in those dynamic parameters are crucial. For example, they allow us to discriminate between different protein environments by means of the EPR spectroscopy using nitroxyl spin labels. In particular, we can assess the mobility of the different elements of secondary structure and probe the constraining effect of the side chains at the surface of the protein. Nowadays molecular dynamics (MD) simulations are able to provide atomic resolution information about molecular motions at time scales up to several microseconds in a reasonable amount of computational time. This allows us to obtain the desired statistics from MD simulations and thus successfully simulate the EPR spectra.

In this contribution, we seek to show that ultra-long MD simulations can be used to draw a connection between the specific structural/dynamic situation of the MTSL probe and the resulting ESR lineshape.

In the work two general approaches to generate ESR spectra are utilized. First uses Redfield theory formalism to convert correlation functions decay rates into spectrum, while second solves Liouville equation numerically using time-dependent Hamiltonian. Both methods were applied to MTSSL-tagged B1 immunoglobulin-binding domain of protein G (GB1), for which the detailed experimental information is available. The agreement between experimental and simulated spectra verifies MD results.

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# Evolution of quantum systems in environments: perturbation theory for Lindblad-Franke equation

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Evolution of quantum systems is described by Lindblad-Franke equation for density matrix. We seek pointers of this equation: such density matrices (i.e. quantum states) that don’t change over time. Pointers are believed to be the final step in evolution of density matrices of open quantum systems and, consequently, they are expected to reveal decoherence, i.e. the process of system's loss of quantum properties and gaining classical ones. To start with, we look at the pointers of the Liouville–von Neumann part of the equation and next we find how they change after “turning on” the Lindblad-Franke part. It is implemented by means of perturbation theory. The cases of non-degenerate and degenerate Hamiltonians are studied. We further apply our method to concrete physical setups.

This work is done in collaboration with A.A.Andrianov, M.V.Ioffe and O.O.Novikov.

# Random interface growth: Kardar-Parisi-Zhang model
## under influence of a turbulent environment

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Scaling behaviour of randomly growing surfaces (interfaces) in various physical systems (solidification, flame fronts, colloid aggregates, tumors, etc.) is often described by the Kardar-Parisi-Zhang equation [1]. However, the field-theoretic renormalization group analysis of the equation has failed to yield the infrared attractive fixed point connected with the scaling (strong coupling point). So far, only functional renormalization group (also called the ”exact” or ”nonperturbative”) has allowed to calculate the point’s coordinates [2,3]. Thus, the perturbative solution remains elusive. In this paper, the Kardar-Parisi-Zhang equation is augmented by the addition of turbulent motion of the environment modelled by the Navier-Stokes equation. The problem is considered as a renormalizable field theory with four different fields; renormalization constants and scaling exponents are calculated to the first order of a small parameter (”one-loop”-approximation) and compared with the known results.

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# Structure of C*-algebra associated with a metric graph

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An eikonal algebra E(Ω) is a C*-algebra [1] related to a metric graph Ω. It is determined by trajectories and reachable sets of a dynamical system associated with the graph [2,4]. The system describes the waves, which are initiated by boundary controls and propagate into the graph with finite velocity. Motivation and interest to eikonal algebras comes from the inverse problem of reconstruction of the graph via its dynamical and/or spectral boundary inverse data [3]. Algebra E(Ω) is determined by these data. It is demonstrated that complex structure of operator eikonal algebra can be implemented as an orthogonal sum of rather simple algebras of matrix functions which have well-known spectrum (irreducible representations).

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# Evaluation of intra-L-shell transitions isotope shifts of beryllium-like ions

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Nowadays highly charged ions (HCI) provide a vast spectrum of opportunities to examine fine effects in physics. Being from the one hand accessible for theoretical description with high accuracy and from another suitable for high-precision atomic experiments, HCI are mainly used to probe quantum electrodynamics (QED) effects in strong electromagnetic fields, refine fundamental physical constants and nuclear parameters and scrutinize astrophysical observations data.

One of the most challenging to theoretical description contribution to a transition energy is the isotope shift (IS). It consists from two parts: the mass shift (MS) due to a finite nuclear mass effect and field shift (FS) due to a nonzero nuclear size effect. One cannot separate this contributions experimentally and therefore has to rely on theoretical calculations either of MS or FS to extract corresponding contribution from precise atomic spectroscopy. Reliable interpretation of spectrum from faraway cosmic x-ray sources also requires detailed knowledge of IS contribution. In present work we focused on relativistic calculations of intra-L-shell transitions IS of low-$Z$ beryllium-like ions. Full relativistic nuclear recoil theory can be derived only from the basic principles of QED in the form of $\alpha Z$ expansion, which in the lowest relativistic approximation and first order in $m/M$ can be presented in form of the relativistic mass shift Hamiltonian [1]. Within this approximation the IS is calculated with a relativistic many-electron wave function in order to take into account the electron-correlation effect. In the present work configuration interaction method in the basis of Dirac-Fock-Sturm virtual orbitals (CI-DFS) and the many-body perturbation theory (MBPT) symbiosis has been exploited for treating valence-valence and core-valence correlations respectively [2]. Interelectronic interaction corrections has been taken into account within the Breit approximation. Scrupulous analysis of basis set convergence has allowed us to obtain accurate values with uncertainty estimation. The results are in reasonable agreement with the benchmark non-relativistic calculations [3] and are the most accurate relativistic ones.

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# Optimal spline approximation of Legendre polynomials

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In many quantum mechanical calculations in order to get computational savings it is advantageous to use a local basis. Therefore, an optimal spline approximation problem of a specific special function class on such a basis becomes very critical for complex quantum mechanical calculations. In particular, we are interested in approximation of Legendre polynomials. Constructing an asymptotically optimal grid [1, 2] is one of the possible approaches of getting computational advantages and increased accuracy.

Several non-uniform grids are proposed and studied. The accuracy of approximation is illustrated through calculation of the squared angular momentum operator eigenvalues using Hermite splines $S_{5,3}$ and $S_{3,2}$ and orthogonal collocations.

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# Advection of active scalar field near d=2: Renormalization Group approach

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The Renormalization Group approach is applied to the model of the active scalar field advection by an incompressible fluid. The behaviour of the fluid is defined by the Navier-Stokes ensemble with external random thermal-like stirring. It turns out that the model becomes the logarithmic one in the case of the space dimension $d = 2$. Thus, the perturbation theory is built as series in $\varepsilon = d-2$. The coordinates of the fixed points and the critical dimensions are obtained in the leading one-loop result.

# Ground and Excited States of Heavy Diatomic Homonuclear Quasimolecules

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Few-electron diatomic quasimolecules represent the simplest molecular systems. One of the most interesting cases is heavy quasimolecules in which Z>173 ($Z=Z_1+Z_2$ is the total nuclear charge). The electromagnetic field strength in such systems can be high enough to approach the critical field strength in the Schwinger mechanism $E_c = m^2c^3/(\hbar e) \simeq 1.3 \cdot 10^{16}\ V/cm$, i.e. electron-positron pair production becomes possible [1]. In other words, the lowest-lying electronic state is close to "dive" into the Dirac negative-energy continuum at small enough internuclear distances [2, 3]. In this case the parameter $\alpha Z \simeq 1$ is not small ($\alpha$ is the fine-structure constant) so calculations cannot be performed using perturbative theory with this parameter; thus, they should be done to all orders in $\alpha Z$.

We present relativistic calculations of the ground-state energy of one- and two-electron diatomic quasimolecules valid to all orders in $\alpha Z$. The Dirac equation with the exact two-center potential is solved numerically using the dual-kinetic-balance method [4]. The results obtained are compared with the results of the previous calculations [5–7].

For two-electron heavy quasimolecules we evaluate also the electron-electron interaction effect within the rigorous QED approach. In the first order this is one-photon exchange correction which is calculated for the exact two-center potential. To the best of our knowledge, this is the most accurate up-to-date evaluation of the two-electron quasimolecular binding energies.

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# Interaction of Light with Diatomic Quasimolecules in Strong Laser Fields in the Dipole Approximation and Beyond

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There are a number of infrastructure projects worldwide that strive for higher laser intensities [1]. The treatment of light-matter interaction in a relativistic framework is thus a timely issue. In this paper we consider the processes of interaction One-Electron Relativistic Diatomic Quasimolecules with Strong Laser Fields. Using the relativistic Dirac equation, the energies of bound states are calculated for the various molecules. As is known, the Schrödinger equation permits a scaling transformation such that the result will not change. By performing this transformation for equations TDSE and TDDE, we analyze the difference between the energies of the bound states for these equations. Various numerical methods for describing the interaction of quasi-molecules with a laser field are also considered. The applicability of these methods in various approximations for the laser field is estimated [2].

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# Classical and quantum solutions in the one-dimensional Gribov model

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V.N. Gribov proposed the following model in 1967 [1]:

$$L = \frac{1}{2}\left(\varphi^{+}\partial_{y}\varphi - \varphi\partial_{y}\varphi^{+}\right) - \mu\varphi^{+}\varphi - \alpha'^{(\vec{\nabla}\varphi^{+},\vec{\nabla}\varphi)} + i\lambda\varphi^{+}(\varphi^{+} + \varphi)\varphi \ (1)$$

Where φ is a complex field, that is a function of 2-d real spatial variable and y, y=it is imaginary time and is associated with rapidity, μ is a dimensionless mass, λ is a coupling constant. This model was proposed as an effective model of pomeron interaction in QCD. The effective action (1) was derived through the analysis of Feynman diagrams and thus is purely perturbative.

Gribov model was actively researched in the 70-s, for example, in [2] and [3]. Here this model is considered with α'=0 (the so-called "toy model") and classical solutions are given, as are the asymptotics of quantum solutions, with several methods of quantization considered. Also, some attention is given to the spectrum of the model.

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# Hwa-Kardar model of self-organized criticality with a quenched noise

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Hwa-Kardar model of a system in a self-organized critical state with quenched noise is studied by the means of field theoretic renormalization group analysis. The model describes random evolution of some profile (for example surface of sandpile) in *d*-dimensional space with preferred mass transport direction [1]. The critical state of such systems is called self-organized because of lack of tuning parameters controlling the correlation length and time in the model.

The quenched noise is described by the correlation function <ff>~δ(ω) was introduced in work [2] as the way to model random variability of the studied profiles (e.g. growing interface, eroded landscape,etc).

In present work the corresponding stochastic equation reformulated as a flied theoretic model, which is studied in leading order of perturbation theory (one-loop approximation) by coupling constant. It is shown that there is stable fixed point of renormalization group equation, which implies scaling behavior of correlation functions of the model. Corresponding scaling exponents are calculated in first order of ε-expantion.

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# Analysis of plasmonic nanodimer excited by electron beam (EELS) accounting for the presence of longitudinal waves with the Discrete Sources Method

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Rapidly developing field of plasmonics involves a great variety of particle study and particle optimization problems. Especially important are applied problems that are connected to the multiple particle analysis [1]. In order to accurately predict properties of such particle systems and therefore to flexibly optimize and tune their configuration avoiding experimental measurements that can be difficult, precise and powerful numerical techniques are required.

Among all known numerical techniques Discrete Sources Method is known to be one of the most efficient and flexible semi-analytical approaches which is capable of carrying out high performance computations of multiple nanoparticle systems such as dimers, at the same time allowing to properly estimate simulation error *a posteriori* [2]. Recently a new DSM numerical scheme has been sucessfully implemented to specifically simulate small (<10nm) single plasmonic nanoparticles under either plane wave or electron beam (electron energy loss spectroscopy, EELS) excitation with account for nonlocal effect which manifests itself through the presence of the longitudinal waves [3].

Simulation of EELS response and account for nonlocality appear to be crucial factors when working with small plasmonic nanoparticles as they exhibit unique properties which one can not predict with classic electromagnetic theory and which could only be measured experimentally with such high spatial and energy resolution technique as EELS [4]. This work is devoted to the further development of the discussed DSM scheme, and in particular to its extension to nanoparticle systems such as dimers.

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# Quality assurance system for $\Lambda^0$ reconstruction in the BM@N experiment

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High density baryonic matter can be obtained under conditions available for NICA project and it makes possible for quark-gluon plasma to be studied there, which is a significant aim of experiments at the facility [1]. Theory predicts that the strangeness would increase in heavy-ion induced interactions, and consequently the study of strange particles in these processes might be of interest as an increase of strangeness might serve as a signature for deconfinement phase transition to the state of quark-gluon plasma. Particularly, being able to detect $\Lambda^0$ hyperons would provide a possibility to indicate this phase transition [2].

The process of converting the electronic signals produced by detectors to the information about particles in the experiment is called particle reconstruction. The BmnRoot framework used for experimental data processing in the BM@N experiment has $\Lambda^0$ reconstruction algorithms implemented. However, these algorithms require testing with Monte Carlo simulation.

To test the performance of $\Lambda^0$ reconstruction algorithms the quality assurance module was implemented in the BmnRoot framework. The quality assurance system deals with the information obtained from Monte Carlo simulation, as well as with the information obtained from existing algorithms of $\Lambda^0$ hyperon reconstruction. The module plots histograms to empower one to study how a geometry of the experiment is suitable for $\Lambda^0$ reconstruction in geometry analysis part, and how $\Lambda^0$ reconstruction algorithms are efficient upon a fixed geometry in reconstruction analysis part. In geometry analysis these histograms depict momentum, pseudorapidity, angle, rapidity and momentum axial projections distributions of the number of $\Lambda^0$ with both of its charged decay products having at least four hits. In reconstruction analysis the same distributions are plotted for the number of actually reconstructed $\Lambda^0$. Not less important quantity being a ratio to the number of totally simulated $\Lambda^0$ is called efficiency. Distributions of it were also plotted for both geometry and reconstruction analysis.

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# On homogenization of periodic hyperbolic systems

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The talk is devoted to homogenization of solutions of periodic hyperbolic systems with rapidly oscillating coefficients. Classical results in homogenization theory looks as the convergence of solutions of the problem with rapidly oscillating coefficients to the solution of the so-called effective problem with constant coefficients. The constants in the corresponding error estimates depend on the differential operator, the lattice of periodicity, and the initial data somehow.

We are interested in the operator error estimates. In such estimates, dependence on the initial data in the error estimates is explicit: we have the norm of the data in error estimate. So, these estimates can be rewritten in operator terms.

The principal term of approximation for the solution of periodic hyperbolic systems was obtained by M. Sh. Birman and T. A. Suslina (2008). Our main result is approximation of solution in the energy norm. The corrector is taken into account. To obtain this approximation we have to assume that the initial data for the solution is equal to zero. The result can be written as approximation of the operator sine in the uniform operator topology with the precise order error estimate.

We use the spectral approach to homogenization problems developed by M. Sh. Birman and T. A. Suslina. The method is based on the scaling transformation, the Floquet-Bloch theory, and the analytic perturbation theory. It turns out that homogenization is a spectral threshold effect at the bottom of the spectrum.

More details: arXiv:1705.02531.

# Weak multiplexing in neural networks

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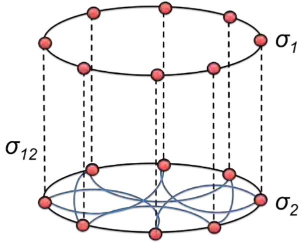
Multiplexing is an important concept in computational modelling of networks, which allows us to study layer-to-layer interactions [1]. By using the model FitzHugh-Nagumo of a biological neuron, we created a two-layer system with nonlocal coupling in the oscillatory regime (Fig.1). By investigating such system, we were able to study the effect of weak multiplexing, i.e., when the coupling between the layers is smaller than that within the layers, on the existence of chimera states. We demonstrate new strategies of control for such spatial-temporal patterns, where desired patterns in one layer can be achieved without changing the parameters of the other layer. These phenomena are shown not only for a case of weak multiplexing between the layers, but also for the strong coupling case, when the interlayer coupling strength is equal to intralayer. It has been observed that in the case of coupling range mismatch between the layers, weak multiplexing leads to the appearance of chimera states, which exhibit different shapes of the mean velocity profile for parameter ranges where they do not exist in isolation. Moreover, we show that introducing coupling strength mismatch between the layers can in some cases suppress chimera states and induce various other regimes such as in-phase synchronization or two-headed chimeras. Interestingly, small intra-layer coupling strength leads to the appearance solitary states throughout the whole network.



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# Partition Function of the Six-vertex Model with Domain Wall Boundary Conditions with Free Boundary

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The six-vertex model (also known as a "square ice") is an important example of a statistical mechanics model whose Boltzmann weights obey the Yang-Baxter relation [1]. This relation insures integrability of the model, which means that the partition function (and correlation functions) can be evaluated exactly, in a closed form. As a model of statistical mechanics, the six-vertex model is extremely interesting by a nontrivial influence of boundary conditions on its thermodynamic properties. Under certain boundary conditions spacial separation of phases may be observed. This is a well-known result for the model on an $N$ x $N$ square lattice with the so-called domain wall boundary conditions (DWBC) [2].

The present study is aimed towards extension of these results on the case of an $N$ x $M$ square lattice where the DWBC are imposed on three boundaries of the lattice and with one boundary having free (or open) conditions. The free boundary conditions mean that the summation of all possible spin configurations is performed. Our main result here is about the partition function of both inhomogeneous and homogeneous six-vertex models with such a partial DWBC in the case of an $N$ x ($N$ - 1) lattice. The partition function is represented as an $N$ x $N$ determinant, similarly to the famous Izergin-Korepin determinant for the usual DWBC case, but with the entries of the last column properly modified. We also discuss a relation of this result to certain boundary correlation function of the six-vertex model with DWBC, which was obtained previously in [3].

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# Contributions of Penguin Operators from Flavor-Changing Neutral Current Hamiltonians to Rare Semileptonic B-Decays

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Modern accelerator experiments are devoted to the study of the dynamics of decays and processes of particle production within the framework of the Standard Model and searches for effects of the so-called «New Physics» [1].

Rare semileptonic decays of *B*-mesons, in particular, $B \to K^* \ell^+ \ell^-$, where $\ell$ is the charged lepton, are theoretically described by the effective Hamiltonians worked out for the $b \to s$ and $b \to d$ transitions. Flavor-changing neutral current operators entering the Hamiltonians can be divided into tree, strong- and electroweak penguins, electromagnetic, chromomagnetic, and semileptonic ones [2].

Relative probabilities of such decays are simple in terms of effective Wilson coefficients, but the structure of these coefficients becomes more and more complicated after taking into account NLO and NNLO radiative corrections due to strong interactions. In particular, in the NLO the radiative corrections occurring due to the four-quark operators, are described by two-loop Feynman diagrams. As one-loop parts, they contain diagrams of the $b \to s + g^*$ and $b \to s + g^* + \gamma^*$ transitions, where $g^*$ and $\gamma^*$ are virtual gluon and photon, respectively.

Calculations of the tree and penguin operators' contributions to the effective $b \to s + g^*$ and $b \to s + g^* + \gamma^*$ vertices induced by the $b \to s$ transition are the necessary ingredient for calculating the $b \to s \ell^+ \ell^-$ in NLO. Our results for the effective vertices with the tree operators' insertion are in agreement with [3] and also include the generalization connected with the inclusion of the penguin operators into consideration. Corresponding two-loop penguin contributions to the $b \to s \ell^+ \ell^-$ transition are under study.

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# Particle angular correlations in proton-proton collisions in the model with interaction of quark-gluon strings

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The study of correlations in proton-proton collisions at the LHC provides important tests for the predictions of quantum chromodynamics and new information about mechanisms of hadron production at low transverse momenta. In 2010, the CMS collaboration observed the so-called near-side ridge in the analysis of two-particle correlation functions in p-p collisions - an increased formation of pairs of particles with a close azimuthal angle, but with large rapidity intervals between them [1]. One of the possible reasons for its appearance is the formation of quark-gluon plasma and elliptic flow in it. Another scenario is the interaction of glasma flux tubes (strings) - gluon force fields stretched between pairs of quarks. In this work, study of the near-side ridge effect in the correlation functions was performed in the PYTHIA monte-carlo generator with the built-in effect of string shoving [2]. It is shown how parameters of this model, namely, the string radius and the strength of string interaction influence the ridge effect as well as multiplicity distribution and average transverse momentum of the particles.

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# Monte-Carlo study of long-range correlations of average transverse momentum and multiplicity for strange particles in pp-collisions at the LHC energies

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Nowadays one of the main directions of researches of high-energy physics is the study of quark-gluon plasma (QGP) – super-hot and superdence state of strongly interacting matter. Some estimators of QGP formation were recently obtained in high-energy *pp*-collisions at the LHC [1], so the interest in study of processes occurring in these collisions has increased. One of the instruments of study of high-energy particle collisions is so called long-range correlations – correlations between quantities observable in different (pseudo)rapidity intervals – forward and backward (pseudo)rapidity windows, - separated by some gap.

Long-range correlations between average transverse momentum $\langle p_T \rangle$ and multiplicity $n$ for strange particles (on the examples of K-mesons and Lambda-hyperons) in *pp*-collisions in $\sqrt{s} = 7$ TeV are analyzed with the PYTHIA 8 event generator [2] with the rope hadronization mechanism [3, 4] turned on. The dependencies of correlation coefficients $b_{n\text{-}n}$, $b_{p_T\text{-}n}$ and $b_{p_T\text{-}p_T}$ on the gap between forward and backward pseudorapidity windows and on a width of the forward pseudorapidity window are studied. The behavior of correlation coefficients for strange particles is compared with the behavior of correlation coefficients for charged particles.

It is demonstrated that for all studied types of particles positive $n$-$n$, $p_T$-$n$ and $p_T$-$p_T$ correlations are observed. The correlation coefficients of strange particles in each of the considered cases are noticeably less than the correlation coefficients of charged particles. The difference of the behavior of the correlation coefficients of charged particles and strange particles is small. The obtained results do not contradict the model of color string fusion.

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# Magnetic Properties of Fe-doped $LaGaO_3$ and $LaAlO_3$: First-Principles Study

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Perovskite-type oxides have recently attracted great attention due to their wide range of applications as advanced materials for solid oxide fuel cells, sensors, electrochemical devices, etc. It was shown that Fe doping in the lanthanum gallate against lanthanum aluminate leads to the formation of Fe-clusters. This becomes a reason of differences in the magnetic properties of two solid solutions [1]. In this work we present a first principles-based approach for modeling of the properties of solid solutions.

Calculations were performed using CRYSTAL14 computer code within CO LCAO approximation. Our research shows that hybrid 9% HF-DFT functional PBE [2] gives the best description of properties of the bulk crystals. We used 2×2×2 supercell to model cubic solid solutions. All the possible configurations of a solid solution with different spin distribution were split into symmetry independent classes (SIC). Optimized geometry, energy and electron properties were calculated for the representative structure of each class. We estimated statistical weights of the obtained structures with the specific local magnetic ordering to find out their probabilities.

We verified the computational scheme by calculations of pure crystals $LaGaO_3$, $LaAlO_3$ and $LaFeO_3$ in three phases (*Pbnm*, *R*-3*c*, *Pm*-3*m*). Further calculations were performed for 27 obtained structures for both $LaGa_{0.5}Fe_{0.5}O_3$ and $LaAl_{0.5}Fe_{0.5}O_3$. It was shown that spin polarization affects the local structure of doped lanthanum gallate and lanthanum aluminate differently. Estimation of average projection of magnetic moment per cell was based on the structure probabilities. We used Ising model to obtain values of the magnetic coupling constants ($J_{Fe\text{-}Fe}$) for both solid solutions. The equal values ($J_{Fe\text{-}Fe} = -0.0105$ eV for $LaAl_{0.5}Fe_{0.5}O_3$ and $J_{Fe\text{-}Fe} = -0.0102$ eV for $LaGa_{0.5}Fe_{0.5}O_3$) confirm the chosen model is appropriate.

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# Influence of elastic spherical inclusions onto nonlinear elastic moduli of a composite

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Currently, composite materials are becoming increasingly popular. It was experimentally shown that at a certain combination of parameters of a base material, the matrix, and those of inclusions, and at low concentration of inclusions, the rigidity of the resulting composite rises noticeably. The linear elastic moduli of composites can be both reliably measured and predicted theoretically. While the nonlinear elastic moduli of a composite can only be determined experimentally, and with a large measurement error. No theory has been developed yet for their estimation. That is why it is of interest to obtain expressions allowing for their estimation from theoretical considerations.

In this paper we demonstrate the applicability of the linear Eshelby theory [1] (which solves the problem of an inclusion in a linear matrix) for determining nonlinear elastic moduli — l, m, n — the so-called Murnaghan moduli, in the case of a low concentration of elastic spherical nanoparticles in an elastic nonlinear matrix. For spherical nanoparticles, the nonlinear effective elastic moduli of a nanocomposite were shown to have the following form:

$$\begin{pmatrix} l_{eff} \\ m_{eff} \\ n_{eff} \end{pmatrix} = \begin{pmatrix} l_0 \\ m_0 \\ n_0 \end{pmatrix} + c\mathbf{P}^0 \begin{pmatrix} l_0 \\ m_0 \\ n_0 \end{pmatrix} + c\mathbf{P}^1 \begin{pmatrix} l_1 \\ m_1 \\ n_1 \end{pmatrix} + c \begin{pmatrix} \mathcal{L} \\ \mathcal{M} \\ \mathcal{N} \end{pmatrix} + O(c^2).$$

Where the matrices $\mathbf{P}^0$, $\mathbf{P}^1$ and vector $(\mathcal{L}, \mathcal{M}, \mathcal{N})^T$ depend on the linear moduli of the matrix $K_0$, $\upsilon_0$ and nanoparticles $K_1$, $\upsilon_1$, and c is concentration of inclusions. Note that nanoinclusions will necessarily create non-linear moduli in the composite, even if the matrix did not have them. This occurs due to the so-called geometric nonlinearity and inhomogeneity of a medium.

A numerical modelling was performed to check the results obtained. The results of theoretical calculations were shown to be in a good correspondence with those of numerical experiments, within the required accuracy to nonlinear terms in the concentration of inclusions. The results obtained can be of use for evaluation of the resulting elastic properties of composites prior to manufacturing, in order to determine the required concentration of nanoparticles providing the desired parameters of a composite.

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# Parameterization of the Corey model on the oil well water cut data

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In the oil industry, one of the most important characteristics of a well is its water cut indicator, which characterizes the ratio of water and oil in the total volume of produced fluid. According to its time dependence, it is possible to predict the further operation of the well. The temporal dependence of water cut from stock production can be well described by a three-parameter model based on Corey correlations [1]. Parameterization of the model is actually a search for the minimum of the objective function on real data and finding three unknown parameters. However, the original data can be very noisy, which greatly complicates the task. Pre-processing (filtering) data needed to successfully minimize the functionality. At the same time, the main trend of dependence should not change, and outliers should smooth.

The main purpose of this work was the implementation of adaptive filtering of source data. It was used two well-known filter: the Kalman filter [2] and the Savitsky-Golay filter [3]. Then the model was optimized using a genetic algorithm on the filtered data and three unknown parameters of the Corey model were found for each well.

It has been shown that both proposed options for filtering the source data successfully cope with their task. The main trend of the dependence did not change, while the minimum of the specified functionality detected more quickly on the filtered data in comparison with unfiltered data.

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# Asymptotically optimal grids for modeling single active electron atoms

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An efficient local representation of the wave function might give a significant computational advantage when solving few-body quantum mechanical problems. For instance, an accurate representation of the wave function in the region of the Coulomb tail is needed to represent single active electron atomic states.

One way to get an accurate spline approximation without significant computational costs is to find an optimal grid [1]. In this research the optimal grid for the two-body Coulomb problem is constructed. We also test the optimal Coulomb grid with model potentials for alkali atoms [2]. Using Hermit splines and orthogonal collocations we show that the grid optimized for the Coulomb problem also produces rapidly convergent results for single active electron models of alkali atoms.

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# Y-junction of Luttinger liquid quantum wires: equivalent field theory, conductance

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Quantum wires are the application of one dimensional interacting fermions. Fermions in wire are described by the model of Luttinger liquid. For wires without impurity conductivity can be obtained either by the exact solution or with the use of bosonization. However, these approaches are complicated for wire with impurities. Based on the exact solution of the Schwinger model, we can clearly find the Green's function for the wire with an impurity or for connected multiple wires. The result for the two wires was obtained by this technic [1]. This theory is consistent with the Bosonization approach in the first-order and higher orders extend that method. For the theory, the renormalization group equations were obtained, which were used for calculation of conductivity up to fourth-order perturbation theory.

Here we extend the method of exact solutions to the case of three or four wires. With the help of functional integration the equivalent one-dimensional field theory is built, in which the field is the phase jump of the wave function at the point of junction. In this theory, the conductivity is calculated up to second-order perturbation theory in the small interaction between electrons. The interesting features of the theory are dimensionless fields and, consequently, infinite number of terms in the Lagrangian.

Full effective action and first order sum of logs are obtained. The full analysis of the system is made (via renormalization group methods).

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# Decoherence of homogeneous modes during inflation

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During inflation the universe rapidly expands and the observed classical distribution of inhomogeneities originates from the substantially non-classical state. The problem of transition from quantum to classical behavior can be solved in the context of the theory of decoherence induced by environment [1]. The essence of this phenomenon is that the quantum degrees of freedom of the system are entangled with the degrees of freedom of the environment, which leads to the suppression of interference effects and the classicalisation of the system.

In cosmological context, the transition to classical behavior is studied within the Wheeler-DeWitt approach with small inhomogeneous perturbations considered over quantized homogeneous background. The Wheeler-DeWitt equation is solved in the Born-Oppenheimer approximation. Using this approximation, one can represent the wave function as a product of homogeneous and inhomogeneous parts. Inhomogeneous wave function is associated with QFT approach on a classical curved background and homogeneous part provides probability amplitude for different backgrounds. The decoherence process itself is observed by studying the corresponding density matrix.

In this paper we discuss the decoherence of background degrees of freedom due to the loss of information about modes going beyond the cosmological horizon while mantaining the full information about the short wavelength perturbations. We demonstrate the classicalization process of the quantum state of inhomogeneities of the universe.

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# Crystal bases for spin chains in the AdS/CFT correspondence

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AdS/CFT correspondence is a famous conjecture, which states the relationship between some types of string theory in anti-de Sitter space and corresponding conformal field theories on its boundary. The duality between IIB string theory inside $AdS_5$ x $S^5$ and N = 4 supersymmetric Yang-Mills theory is one of the most examined and most well-known examples where correspondence takes place.

Despite being a conjecture, the case we are to consider took a huge amount of tests. One of them is to compare spectrum of anomalous dimensions of operators in N = 4 SYM theory with spectrum of energies of string configurations which correspond to the latter. We considered single-trace operators consisting of fields from su(3) subsector of N = 4 SYM at one loop and strings propagating in $S^5$ with huge angular momenta.

In [1] it was shown that computing anomalous dimensions of such operators is equivalent to solving spectrum of a certain spin chain. In order to test the conjecture and meet the condition on huge angular momentum at the string side, one needs to consider long spin chains which, in our case, is equivalent to huge tensor powers of su(3) fundamental representation.

Crystal bases provide us with a combinatorial tool, which is helpful for computing tensor product decomposition of Lie algebra's representations. We present a program realization, which decomposes tensor powers of su(3) fundamental representation, builds crystal graphs for irreducible components and derives basis of representation space. The latter can be used for diagonalizing matrix of anomalous dimensions and obtaining its spectrum.

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# Neural networks based methods for solving the equations of quantum mechanics: a study on optimization algorithms

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In this work we study derivative-free optimization algorithms aimed for high dimensional optimization problems that arise in the context of solving differential equations with neural networks. We solve the differential equation for one-dimensional harmonic oscillator using a neural network with one hidden layer. To train the neural network we use the Nelder-Mead simplex method [1].

A new convergence criterion for the Nelder-Mead simplex method is proposed and compared with conventional convergence criteria. We also study the method of differential evolution and compare it with the simplex method.

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# Investigation of Deep Learning methods for the classification of events in the NOvA experiment

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With the rise of questions concerning the problems of the theory behind the phenomenon of neutrino oscillations, more and more neutrino experiments are under development and underway. One such experiment, NOvA, is supposed to tell the scientific community more about $\nu_\mu \rightarrow \nu_e$ (as well as anti-$\nu_\mu \rightarrow$ anti-$\nu_e$) oscillations, $\nu_\mu$ and anti-$\nu_\mu$ disappearance channels, to determine the order of neutrino masses, CP-violation phase in the lepton sector, and to measure precisely mixing angles, as well as $\Delta m^2$ (squared mass differences) [1]. A brandnew approach of using convolutional neural networks has been applied in order to improve the quality of NOvA's data analysis, bypassing the standard event reconstruction procedures [2]. The idea of combining the reconstruction with Convolutional Neural Networks (CNN) is interesting, as it may help with increasing the degree of precision and performance speed. Since the data is generally composed of particle tracks, emitted from an interaction point, we have attempted to train NOvA CNN on images that have had a polar transformation applied to each event, with the transformation origin located at the event's interaction vertex. In this way tracks emitted from the vertex will be represented by a horizontal line, perhaps presenting an easier data set for the network to learn from. We have shown that such a dataset decreases the overtraining of the network, though, slightly reducing the validation accuracy.

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# Influence of compressibility effect on superfluid state transition in $He_4$

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According to the classical works it is supposed that the critical dynamics near the lambda point is described by F or E stochastic model. In these models it is considered that influence of compressibility in dynamic description is inessential. In this work we tried to verify validity of using these models. Liquid helium was described using model F of critical dynamic with included velocity field. We checked influence of fields appeared because of compressibility effect using the analysis of canonical dimensions. The results obtained contradict the basic statement about inessential of compressibility in dynamic and in fact are nontrivial. Moreover the results shows us that we have to include appeared fields. It is also shown that the dynamics considered to be described by the stochastic model A.

# Ground-state g factor of middle-Z boronlike ions

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The past two decades have been marked by intensive development of the g-factor studies in highly charged ions [1,2]. Independent determination of the fine structure constant α is possible in g-factor studies with high-Z or middle-Z boronlike, lithiumlike and hydrogenlike ions [3,4]. Experimental precision has reached the level of $10^{-9}$–$10^{-11}$ for hydrogenlike and lithiumlike ions. Cooperative experimental and theoretical work lead to the most accurate up-to-date value of the electron mass [5]. The most stringent test of the many electron QED effects in the presence of magnetic field has been achieved with middle-Z lithiumlike ions [6]. The ARTEMIS experiment presently implemented at GSI aims at measurement of the g factors of both ground and first excited states of boronlike argon [7].

We present the results for the ground-state g factor of boronlike ions in the range Z = 10–20. The first-order interelectronic interaction and the self-energy corrections are evaluated within the rigorous QED approach in the effective screening potential. The second-order interelectronic interaction is considered within the Breit approximation. The nuclear recoil effect is also taken into account. The results for the ground-state g factor of boronlike ions in the range Z = 10–20 are presented and compared to the previous calculations.

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# H. Soft matter
# (biophysics, polymer physics, liquid crystalls, colloids ...)

# Study of DNA interaction with new Zn(II) phenanthrocyanine complexes

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Metal complexes are widely used as antitumor, antimicrobial and antifungal drugs, artificial nuclease, photosensitizers. This is the reason for the synthesis of new complex compounds and studying their interaction with DNA.

In this work two new compounds have been studied — complexes of Zn (II) with 1,10-phenanthroline derivatives: bis- (1,10-phenanthroline) - (1,10-phenanthrocyanine) -dizinc (II) acetate (Zn7) and its precursor bis- (1,10-phenanthroline) -zinc (II) acetate (Zn8). The investigations were carried out by the methods of absorption and fluorescence spectroscopy, as well as spectrophotometric melting. Changes in the spectral properties of compounds at pH 3-1.5 can be caused by the dissociation of one of the phenanthroline molecules from the metal complex and its protonation, and at pH 8 – 12 — by replacing of the water molecules in the metal complex with $OH^-$ ions.

Spectral data indicate the complexation of the testing compounds with DNA. One of the supposed types of binding is intercalation. Saturation of binding does not occur at $0.1 < r < 18.4$ for Zn8 and at $0.1 < r < 1.67$ for Zn7. It is possible to form secondary (dimeric) complexes of test compounds on DNA. The formation of a complex with DNA leads to quenching of the fluorescence of Zn7 and Zn8. This allows us to consider the possibility of using these compounds for photodynamic therapy.

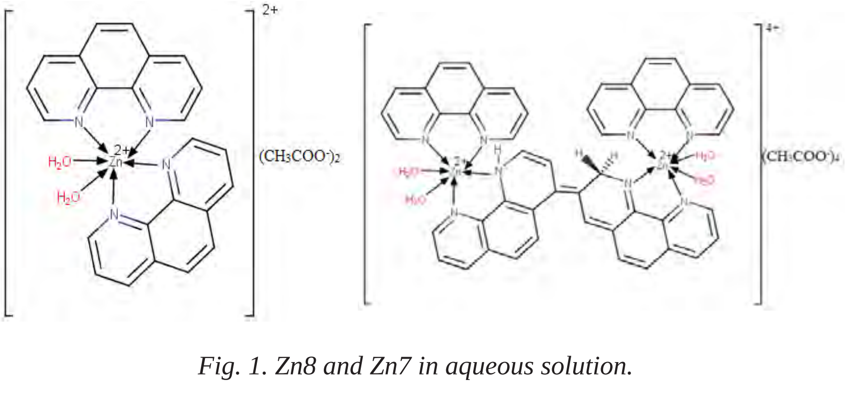

*Fig. 1. Zn8 and Zn7 in aqueous solution.*

# Analysis of DNA interaction with silver and gold ions in solution

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Nanoparticles of noble metals (gold and silver) have unique physicochemical properties and enhance therapeutic effect in cancer treatment. One of the popular way to form nanoparticles is the reduction of ions in a solution. The connection of nanoparticles with nucleic acids allows fabricating new systems with amazing properties. Therefore, it is logical to regard the formation of DNA complexes with gold and silver ions in water-salt solutions and to test the reduction of metal ions after their binding to DNA.

The result of DNA binding with silver and gold ions show that the main position for the formation of stable complexes is GC pair in a major groove of macromolecule. It was shown that the concentration of silver and gold compounds in DNA solutions determines the type of binding. For example, at low ions concentration the binding does not accompany with the destabilization of DNA secondary structure. In contrast to that, at high concentration of ions the local unwinding of double helix with the destruction of hydrogen bonds between complementary base pairs was observed. The absorption spectra of DNA in complexes with gold ($KAuCl_4$, $HAuCl_4$) and silver ($AgNO_3$) compounds show similar changes and point to the N7 guanine in a major DNA groove as a main binding position. We can suggest the transformation of the coordination sphere of Au ion due to aquatation with the change of the charge of complex ion from $2^-$ to $2^+$. CD spectra confirm the formation of Au complexes with DNA bases. However, the CD spectra of DNA with the silver complexes have more significant changes. In addition, hydrodynamic methods (low gradient viscometry, flow birefringence) were used to obtain information about the tertiary DNA structure. The volume of molecular coil and DNA persistent length were determined. It was shown that the volume of the macromolecule decreases during the interaction with Au and Ag compounds. The reduction of gold and silver ions after their binding to DNA bases was carried out and the result of this reduction was studied.

# Conformational and optical characteristics of cationic copolymers in solution

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In recent decades, there is a great interest in cationic polyelectrolytes due to their important role in the development and implementation of new methods and approaches for the creation of nanostructures and multicomponent systems. These objects can formed interpolyelectrolyte complexes with biological active macromolecules.

In this study properties of poly(dimethyl-(2-aminoethyl)methacrylate-co(2-aminoethyl)methacrylate) and poly(methyl(2-aminoethyl)methacrylate-co-(2-aminoethyl)methacrylate) (Fig.1) were investigated by the classical hydrodynamic methods such as viscometry, velocity sedimentation and translation diffusion, flow birefringence. The characteristic values of the intrinsic viscosity, translational diffusion coefficients and sedimentation coefficients were found. The values of the molar masses and hydrodynamic invariant were calculated for all investigated objects.

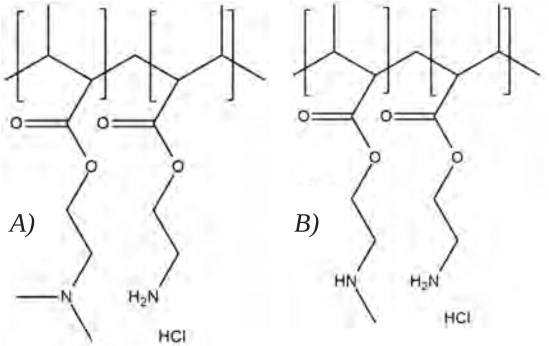

*Fig. 1. Chemical structures of A) p(DMAEMA-co-AEMA) and B) p(MAEMA-co-AEMA).*

**Acknowledgements.** This research was supported by a grant from the Russian Science Foundation (project №16-13-10148). A part of experiments was performed by the equipment at the "Center for diagnosis of functional materials in medicine, pharmacology and nanoelectronics of Saint-Petersburg State University".

# Physico-chemical properties of thermoresponsive amphiphilic star-shaped copolymers

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Calixarenes are often used as a basis for creating supramolecular nanostructures, "smart" systems and materials for medicine and pharmacology. There is a possibility of modification the lower bands of calixarenes by a wide variety of radicals, thereby controlling the potential capability of intermolecular aggregation (complexation). The variations of radicals' structures can consequently cause significant changes in the conformational and physical characteristics of macromolecules.

The molecular properties of thiacalix[4]arenes poly(undekanoyl-2-etiloxazoline) and poly(undekanoyl-2-izopropiloxazoline) in water and tetrahydrofuran were studied in present work.

Classical self-sufficient hydrodynamic approach based on the implementing of the fundamental experimental techniques, such as sedimentation, dynamic light scattering, viscometry and densitometry, enable to carry out the detailed analysis of the studying systems.

The polymer-solvent interactions have been analyzed into two different media tetrahydrofuran and water. Thus, the significant influence of thermodynamic quality of solvents was observed. The values of the lower critical temperature of water solutions were determined experimentally.

It was found that the individual macromolecules with the average hydrodynamic radius Rh ~ 2-3 nm are present in both solvents. Considerably large aggregates (5-7 nm) were observed in water solutions due to the results of dynamic light scattering and analytical ultracentrifugation. The presence of particles with a larger hydrodynamic radius in water solutions is, probably, related with intermolecular aggregation of the studied polymers.

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# Synthesis of SPIONs in inverted nanoemulsion system and their extraction into aqueous media through phase transfer

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The goal of this work was to synthesize stable nanoemulsion based on superparamagnetic iron oxide particles (SPIONs) for MRI diagnostics. Magnetic nanoemulsions with high Fe content have been prepared at two steps. At first, the magnetic nanoparticles were prepared according the Massart method in water. Nanocrystals of magnetite were formed by addition of ammonium hydroxide to the solution of $FeCl_3$ and $FeSO_4$ at ambient temperature. Then the suspension of $Fe_3O_4$ nanoparticles was mixed with the microemulsion, stabilized by nonionic surfactant Tween81 (HLB10) and sonicated at 22 KHz. The ternary system Tridecane-water-Tween81 has been able to solubilize SPIONs. Phase diagram has a large area representing inverted micelles loaded by SPIONs. Surfactant layer coated the surface of nanoparticles. The composition ratio provides the formation of the homogeneous system resulting in stable suspension for month storage.

The prepared nanoparticles were in superparamagnetic state as follows from the absence of appreciable magnetic hysteresis. The presence of large magnetic moment was confirmed by measurement of magnetic relaxation of protons at resonance frequency 300 MHz. The microemulsion loaded by iron oxide nanoparticles can be considered a magnetic ferrofluid. Iron oxide nanoparticles shorten the spin-spin relaxation time from seconds to 1 ms and give rise decrease of intensity of MRI images in phantom study.

For biological experiments, the prepared SPIONs were transferred into aqueous media by introduction of a water-soluble surfactant. To achieve the phase inversion, we chose several commercial surfactants with HLB ranging from 13 to 19: Pluronic L64, Tween 20, Triton N-101 and MYRJ 59, and added them in 1:1 ratio into the hydrophobic magnetic microemulsion. The positive result of phase inversion is demonstrated by the magnetophoresis of the $Fe_3O_4$ nanoparticles under influence of constant Nd magnet. Thus, we have a magnetic nanoparticles coated by a layer of water in stabilized emulsion form. This nanoemulsion system can be used in MRI study as contrast enhancer.

# Development of new approaches to diagnose preeclampsia

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Preeclampsia (PE) is a human-specific pregnancy disorder of unknown etiology and a leading contributor to maternal and perinatal mortality worldwide [1]. The clinical symptoms appear after 20 weeks of gestation and include hypertension and proteinuria. Nowadays there is no cure other than delivery and no reliable laboratory diagnostic methods of this disease.

Earlier Buhimschi et al. (2014) found amyloid-like aggregates in the placenta and urine samples of pregnant women with PE. Besides, the urine samples exhibit congophilia, affinity for the amyloidophilic dye Congo Red (CR). The researchers report that the urine congophilic material includes proteins like SERPINA1, albumin, and Alzheimer's β-amyloid. They designed a simple method (Congo Red Dot (CRD) test) that consists of mixing urine with Congo red, spotting on a nitrocellulose membrane and washing in methanol. The CRD procedure carries diagnostic and prognostic potential for preeclampsia.

In our research the CRD procedure proposed by Buhimschi et al. was optimized and applied for the following investigations. We have estimated efficiency of CRD test as alternative to standard approach in the diagnosis of PE. Using the CRD test, we analyzed the urine samples of pregnant women with PE ($n = 25$) and control groups ($n = 25$). For each sample we have calculated the Congo red retention (CRR). It was found that CRR in cases of women with PE is statistically higher compared with the control group. In prospect, the range of CRR values appropriate for PE diagnosis would be determined.

In addition to the CRD test Protein Misfolding Cycling Amplification (PMCA) was used. It was shown that PMCA is capable of increasing the small amounts of beta-amyloid aggregates in cerebrospinal fluid samples to the level suitable for the fluorescence detection using Thioflavin T [2]. We introduced the system for the detection of beta-amyloid aggregates by PMCA in a solution of chemically synthesized beta-amyloid monomers.

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# Confinement effect in layer of lanthanide complex

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An analysis of the experimental data on the optical Δn and dielectric Δε anisotropies [1] of the nematic phase of the metallomesogen at temperatures near the nematic-isotropic phase(N-I) transition using Landau-De Gennes theory of phase transitions is performed. The liquid-crystalline complex studied in this work was tris [1-(4-(4-propylcyclohexyl) phenyl) octane-1, 3-diono] - [5, 5′-di (heptadecyl)-2,2′-bipyridineytterbium[2]. A comparison of the Δε and Δn values of the liquid crystalline phase with the electro-optical constant of the isotropic phase showed that under real experimental conditions the nematic and isotropic phases coexist on an interval of several degrees in the transition region. This is because the temperatures of the N-I transition in the depth of the experimental cell and on its boundary differ. Using the method of polarization microscopy, we determined the temperature of the N-I transition in plane cells of different thicknesses. It was found that the temperature of the phase transition decreases by more than ten degrees with a decrease in the thickness of the metallomesogen layer from 200 to 5 micrometers. This behavior significantly distinguishes liquid-crystalline complexes of lanthanides from calamitic LCs. In calamitcs, the effect begins to appear in the pores with a characteristic size of less than one micrometer [3]. It is possible that for a large confinement the effect is due to the coordination bonds of the metallomesogenic complexes.

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# Synthesis of stable copolymer-coated gold nanoparticles and their complexes with DNA

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Gold nanoparticles (AuNPs) are widely used in different areas because of their unique properties. Efficiency of usage may vary with the size and shape of particles, which depends on synthesis. A new method of creating gold nanoparticles without reducing agent in solutions containing chloroauric acid or its salt and synthetic copolymer (Fig.1) was proposed in this research. The optimal concentrations of components and the exposure time for obtaining homogeneous gold nanoparticles were selected. The fabrication of nanoparticles as well as their stability were investigated by the methods of spectrophotometry and dynamic light scattering. The formation of gene vectors based on DNA-copolymer complexes with the inclusion of AuNPs was tested.

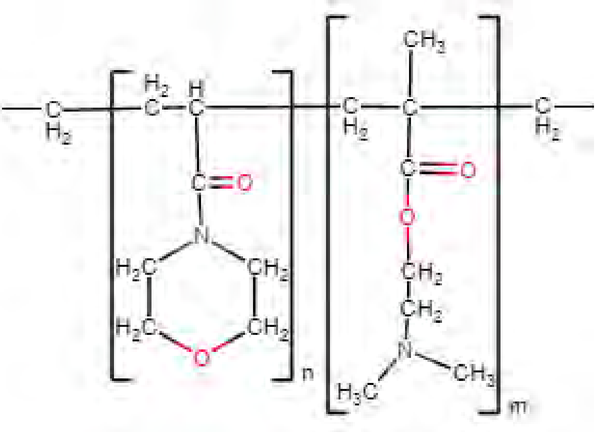

*Fig. 1. Copolymer n = 74, m = 26.*

The interaction between copolymer with AuNPs and DNA with the formation of discrete particles were controlled by spectrophotometry, viscometry and atomic force microscopy.

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# Conjugation of modified Sos1-derived peptide and N-terminal SH3-domain of adapter protein Grb2

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Bioconjugation techniques are widely used in the area of imaging, drug delivery, mapping of protein interactions, etc. One potentially attractive field of research is development of irreversible inhibitors for use in targeted therapy, including covalent peptide ligands.

However, in some cases covalent protein-protein and protein-ligand interactions may lead to significant changes in target protein structure. Such effects are still poorly understood and should be studied by appropriate methods of biophysics and biochemistry. In this context, it should be useful to develop a modeling technique to assess the feasibility of covalent binding and to predict possible changes in target protein structure in response to ligand binding.

For this purpose we have chosen a model system consisting of N-terminal SH3 domain from adapter protein Grb2 and its Sos1-derived (VPPPVPPRRR) peptide ligand containing non-native reactive C-terminal residue (chloroacetyl lysine, X') [1]. Using SDS-PAGE, heteronuclear 2D and 3D NMR spectroscopy and LC-MS/MS technique we performed characterization of both non-covalent and covalent binding in this system. Then, based on our experimental results, we have designed an MD-based protocol to model the conjugation between Sos1X' and Grb2 N-SH3.

A series of MD simulations with the net length of several microseconds led to high-quality atomic models of Grb2 N-SH3 / Sos1X' covalent complexes, which were used to predict NMR chemical shift changes that occur upon the covalent binding. These results were found to be in good agreement with our experimental data. We suggest that the new methodology presented in this work could be used to develop covalent peptide inhibitors for different proteins implicated in human diseases. In particular, this strategy can be used to target extracellular domains of cell-surface receptors, e.g. GPCR family.

The work was supported by the RSF grant 15-14-20038.

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# Synthesis and Application of Metallic Nanoclusters

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Recent advances of nanotechnology have produced a fundamentally new class of fluorescent labels named metallic nanoclusters (NCs). Due to their unique physical and chemical properties, NCs occupy a middle position between individual atoms and nanoparticles and can be applied in various fields of science: medicine, microbiology, chemistry. Singlet oxygen which is generated during luminescence may be used in photochemotherapy to fight cancer. Investigating of metal nanoclusters is young but promising area for research.

Spectrofluorimetry, microscopy and spectrophotometry were the main methods used to study silver and gold nanoclusters synthesized on BSA (bovine serum albumin). Fluorescence emission/excitation and absorption spectra of the nanocluster's were recorded and analyzed. Synthesized nanoclusters were implanted in yeast cells. The success of the experiment was also confirmed on a luminescent microscope. We even could watch cell organelles.

Nanoclusters can be synthesized on different organic bases (e.g. on natural DNA, oligonucleotides, proteins or amino acids, etc). In this research we used BSA but we are going to try other matrixes in the future.

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# Interactions of biomembranes with cellulose. Computer modeling

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Over the last decade, one of the most attractive areas of research is related to cellulose, due to the increase in the number of base-cellulose biomedical applications. One of such possible biomedical applications is wound dressing. The most important point about these applications is that wound dressing are in direct contact with the wound. Consequently, we have interaction between dressing material and the surface of cells or, more precisely, with cell membranes. Thereby, in this work we present the state-of-the-art computer simulations to unlock the behavior of this phenomena i.e., describe the interactions between the model of cell membranes (phospholipid bilayers) and the cellulose crystals.

As a result, we clearly demonstrate that we have a strong attractive interactions between these two groups. Basically, these interactions are due to the presence of hydrogen bonds between phosphate groups of lipids and cellulose's hydroxymethyl/hydroxyl groups. To sum up, our findings contain significant information on the molecular nature of the interaction between phospholipid bilayers and cellulose crystals and can be used for the next step to understanding more about all sides of interaction between cell membranes and with not only the simple cellulose crystals but also with chemical modified cellulose crystals.

**Acknowledgements.** The authors wish to acknowledge the use of the SHARCNET computing facilities (Canada) and the computer cluster of the Institute of Macromolecular Compounds RAS. This work was supported by the Russian Ministry of Education and Science within State Contract 14.W03.31.0014 (megagrant).

# Antioxidant activity and binding of the $C_{60}$-Arg derivative with human serum albumin (HSA)

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Water-soluble derivatives of fullerenes have potential for application in various fields of science and industry in particular in biomedicine due to promising biological activity of such compounds [1-4].

In this work the mechanisms and quantitative parameters of the binding of the $C_{60}$-L-arginine derivative to human serum albumin (HSA), as well as the antioxidant activity of $C_{60}$-L-arginine in the reaction with the stable DPPH (2,2-diphenyl-1-picrylhydrazyl) radical were studied.

The study of the binding of the $C_{60}$-Arg with HSA was performed by recording emission spectra on spectrofluorometer in the wavelength range of 310–450 nm, the excitation wavelength of 290 nm.

The antioxidant activity of the $C_{60}$-Arg was measured spectrophotometrically at the wavelength of 515 nm to obtain the kinetic of the reaction of DPPH radical with $C_{60}$-Arg ($T = 298.15$ K).

The emission spectra of HSA solutions in the absence and in the presence of the $C_{60}$-Arg were obtained. It was shown that the observed spectra correspond to the fluorescence of the residues of tryptophan moiety of HSA. Moreover, the values of quenching ($K_{sv}$) and binding ($K_b$) constants of the $C_{60}$-Arg with HSA were calculated in the temperature range $T = 298.15–308.15$ K. For example, at $T = 298.15$ K $K_{sv}=5.01\pm0.06\cdot10^4$ $M^{-1}$ and $K_b=14.84\pm0.43\cdot10^4$ $M^{-1}$.

It was established that the $C_{60}$-Arg has antioxidant properties. The mechanism for the reaction between $C_{60}$-Arg and DPPH involves two stages: a hydrogen transfer to the DPPH radical (fast stage; $k_1 = 0.0151$ $min^{-1}$), a nucleophilic attack of a C=C bond (rate-determining stage; $k_2 = 0.0038$ $min^{-1}$).

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# Study of SUP35 prion protein aggregation using dynamic light scattering

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Motivation for study of prion proteins is mainly related to their ability to cause a number of neurodegenerative diseases such as Alzheimer’s and Parkinson’s deseases. A common feature of the pathogenesis of these deseases is the forming of amyloids that cause neurocells death. Amyloids are fibrillar filaments formed by functional proteins as a result of their partial unfolding and misassembly .

The yeast protein Sup35 offers a convenient model for studying the mechanisms of amyloid formation and propagation, which can give us a key to understanding such processes for human prion proteins. The process of aggregation have been analyzed using different methods such as microscory, circular dichroism, fluorescence and others. However, the precise mechanism of amyloidogenesis is still unknown.

Dynamic light scattering also can be very useful tool for the aggregation process analysis. It allows to estimate a length distributions of amyloids taken in different time points since the beginning of aggregation. These distributions are in a good agreement with distributions obtained using scanning electron microscopy.

For processing DLS data a number of methods was developed. Using modeling by HYDROPIX program and analytical formulas length dependences of diffusion coefficients of fibrills were obtained. Using the NFM-DS software package the length dependences of differential scattering cross sections of fibrills were obtained by T-matrix method. A program for processing autocorrelation functions by the CONTIN method was developed and verified. This allowed us to describe quantitatively the process of the Sup35 prion protein aggregation.

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# X-ray photoelectron spectroscopy as an instrument for biomolecules analysis

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X-ray photoelectron spectroscopy (XPS) is a widely used method for analyzing surface chemical structure, in most cases this surface is crystalline. At last decades XPS is used also for investigating chemical structure of organic compounds, including biomolecules. As far as the XPS is not common technique for biomolecules structure analysis, biologists and biophysicists are facing a lot of difficulties. The main problems at this field are complexity of biomolecules (its big size and variety of chemical bonds for one chemical element like carbon in organic structures) and insufficient samples purity. These problems cause a lot of fitting mistakes that lead to loss of a huge amount of significant information embedded in the spectra and wrong further data interpretation.

The submitted research provides useful information and clear examples of proper usage XPS as an instrument for investigating chemical structure of biomolecules such as ss-DNA oligonucleotides [1] and bovine serum albumin (BSA) [2] in the macromolecular complex with silver clusters. In the current work the chemical structure of these metalorganic complexes has defined just by XPS technique.

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# Ultrafast dynamics of excited state in cytosine chains

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It is well known that sun light is a mutagenic agent causing various DNA damages. One of the most dangerous DNA changes are so-called cyclobutane pyrimidine dimers (CPDs). Which may cause skin cancer [1]. CPDs and other photoproducts mostly appear from direct interaction of UVB solar radiation with DNA. The reaction of CPD formation proceeds very fast - within ~1 ps [2]. What happens before is vitally important for understanding the basic principles of DNA photochemistry. The primary photoprocesses on femtosecond time scale affecting the efficiency of CPDs formation has therefor been a subject of intense studies during past decade [3].

We have studied the excited state dynamics for neutral single-stranded and hemi-protonated stacking forms of cytosine chains $(dC)_{10}$ using fluorescence up-conversion technique. In most cases the steady-state fluorescence spectra of DNA polymeric forms in general are originate from long-lived species with low fractional amplitudes. In this study fluorescence up-conversion spectra refer to a major fraction of the bases. For the hemi-protonated i-motif form, two fluorescent components have seen in the fluorescence decay curves. The fast component should be attributed to monomer-like emission. The slow component belongs to the excitonic states in hemi-protonated $(dC)_{10}$. We conclude that in $(dC)_{10}$ both local (monomer-like) and delocalized (exciton) states can form from the Frank-Condon state in less than 100 fs.

This work was supported by the RFBR, project No. 18-33-01233.

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# Hydrodynamic properties of chitosans modified with quaternary ammonium

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Polysaccharides are biocompatible polymers, due to this reason they are widely used in medicine and pharmacology, as well as in many other industries. Natural source of chitosan is chitin - the second most common polysaccharide in the biosphere. The combination of availability and such qualities as water solubility and antibacterial activity makes them attractive for use in medicine and pharmacology. Polysaccharides often have to be chemical transformed for practical usage. One of possible chemical modification is the quaternization of the polymer chain, which usually improves water solubility and reduces the dependence of the hydrodynamic parameters of macromolecules on the pH and ionic strength of the solutions.

In this study modified by glycidyl (trimethylammonium) chloride chitosans (using two different techniques) were studied by viscometry, static and dynamic light scattering, ultracentrifugation and translational diffusion. The hydrodynamic and conformational properties of the initial chitosan and its two derivatives obtained by two ways of introducing quaternary amino groups into its side substituents were compared. According to the results of studying it was concluded that quaternization leads to compactification of the polysaccharide chain. This can be explained by changing in the density of the polymer coil, the deterioration of the thermodynamic conditions for the modified chitosan in comparison with the initial analogue in the same solvent, and a slight decrease in its equilibrium rigidity due to a change of contribution of the electrostatic component. It was shown that quaternization method has a significant effect on the hydrodynamic parameters of the polymer chain.

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# Interaction of cis- and trans-DDP with DNA

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Currently, the treatment of cancer is one of the most difficult and urgent medical tasks. Some approaches are based on the application of platinum coordination compounds. Among these drugs the most successful one is dichlorodiammineplatinum(II) (DDP). The *cis*- isomer of DDP is biologically active (this compound is used in medicine) While the *trans*- isomer of DDP demonstrates no biological activity (Fig. 1). It is known that DDP is able to interact with DNA and proteins in living cells. However, many aspects of such interaction remain unclear.

In our work, we studied the interaction of the both DDP isomers with calf thymus DNA using UV spectroscopy. The effect of DDP on the thermal stability of DNA was studied. Also we have optimized the procedure of processing DNA melting curves. All melting temperatures were determined in two different ways: as the midpoint of the melting curve and as the inflection point of the S-shaped curve. It has been shown that the dependence of the melting temperature of DNA (Tm) on the molar ratio of DDP to DNA b.p. (r), is different for *cis*- and *trans*-DDP. In addition, we conducted a series of experiments to study kinetics of the DNA platination. The reaction rate constants for the both isomer were estimated.

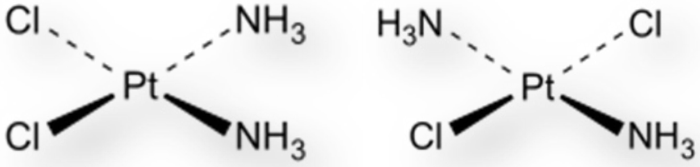

*Fig. 1. Cis- and trans- isomers of DDP.*

# Synthesis of fluorescence silver clusters on tRNA matrix

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Metal clusters are specific class of nanoobjects. In comparison with gold clusters [1], characterized by chemical stability, silver clusters are more interesting for biological application due to their higher fluorescence quantum yield and absorption cross-section. It is well known that silver clusters can be stabilized by many macromolecular matrices, including DNA [2], peptides and proteins [3]. However, there are no literature data on the synthesis of fluorescent metal clusters on transfer RNA (tRNA) as stabilizing matrix.

tRNA is an effective translation adaptor that serves as the physical link between the messenger RNA (mRNA) and the amino acid sequence of protein. Secondary structure of tRNA is usually visualized as a cloverleaf structure (Fig. 1). In our previous work [4], we showed that hairpin-like oligonucleotide structure is the key to formation of fluorescent silver clusters. tRNA contains several hairpins, which could facilitate the clusters formation.

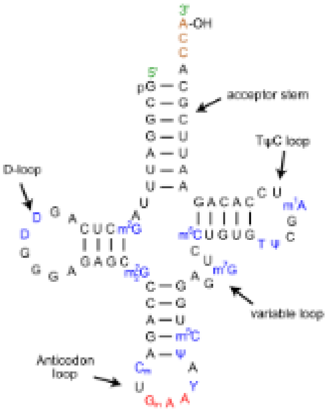

*Fig. 1. Secondary cloverleaf structure of tRNA$^{Phe}$.*

In this study, we use a mixture of 20 tRNA from *E.Coli* (type XX) which can bind with silver clusters obtained by reducing silver ions with sodium borohydride ($NaBH_4$). We obtain several types of the luminescence clusters, emitting in different regions of visible spectrum. For characterization of their photophysical properties, we use steady-state luminescence methods, including fluorescence excitation and emission spectra, lifetime and quantum yield measurements.

This work was supported by RFBR grant 18-33-00603.

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# The applicability of inorganic phospates as an internal standard in IR spectroscopy of protein solutions

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Infrared spectroscopy is one of the most informative experimental approaches to study structure of biological macromolecules, such as proteins and nucleic acids. Recently, the applications of IR spectroscopy of biomolecules in aqueous solutions, based not only on the analysis of the positions of various spectral bands, but also on their intensity became widely spread. Such applications require some sort of internal standard of absorption to be used. In cases when spectra represented by number of well separated bands, such a task can be solved relatively easy. However, the IR spectra of proteins and polypeptides have no bands which could be referred to as internal standard. Our study is devoted to the analysis of applicability of inorganic phosphates as the internal standard in IR spectroscopy of proteins in solution.

Spectral analysis of the solutions containing phosphates in various concentrations was performed. Samples were prepared in $H_2O$ and $D_2O$ solutions. The spectra were recorded using Fourier spectrometer TENSOR27 (Bruker). Based on the analysis of the vibrations in phosphates and water molecules, including those within the hydration layer of phosphate groups the individual bands providing linearity of the absorption upon concentration were identified. Thus we can conclude that it is possible to use salts of a phosphoric acid and buffers on their basis as internal standards of absorption in IR spectroscopic studies of aqueous solutions of proteins.

# Biologically active substances in tea

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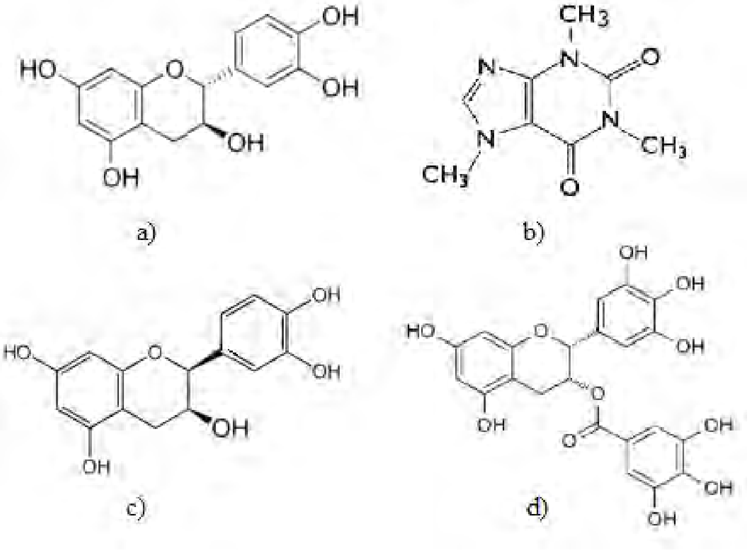
Tea is the most widely consumed drink in the world. Furthermore its consumption is beneficial for some systems of the human body such as the circulatory system, the digestive system, the immunity system. Recent articles have argued for anticarcinogenic effect of tea and besides ability to inhibit cancer growth.

It is caffeine and catechins properties, which are increasingly interesting due to major contribution of this compounds to chemical composition of tea. Using the method of giant Raman scattering and comparing the spectra obtained, presence of caffeine, catechin, epicatechin and epigallocatechin gallat (Fig. 1) was tested in green tea extract. It was established, that the most intense lines in the tea spectrum are determined by contribution of epigallocatechin gallat and epicatechin.



a) b) c) d)

*Fig. 1. Main components of tea: a - epicatechin, b - caffeine, c - catechin, d – epigallocatechin gallat.*

# Modeling of indirect effect of radiation

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Most of radiation-induced DNA damage in cells is caused by an indirect effect of radiation. In the indirect action, free radicals reacting with a DNA molecule are produced due to interaction between ionizing radiation and water or other molecules. Since water constitutes about 70% of cell its contribution should be considered primarily. Products of water radiolysis are shown in Fig. 1.

Series of experiments were carried out to define a contribution of hydrogen peroxide (H2O2) and hydroxyl radical (HO•) to damage of one of the nucleosides of DNA - thymidine. The damage was determined analyzing absorption spectra of thymidine solution, consequently, the number of chromophores before and after interaction with a radiolysis product. It was estimated that influence of hydroxyl radicals plays a huge role in DNA damage compared with molecules of hydrogen peroxide.

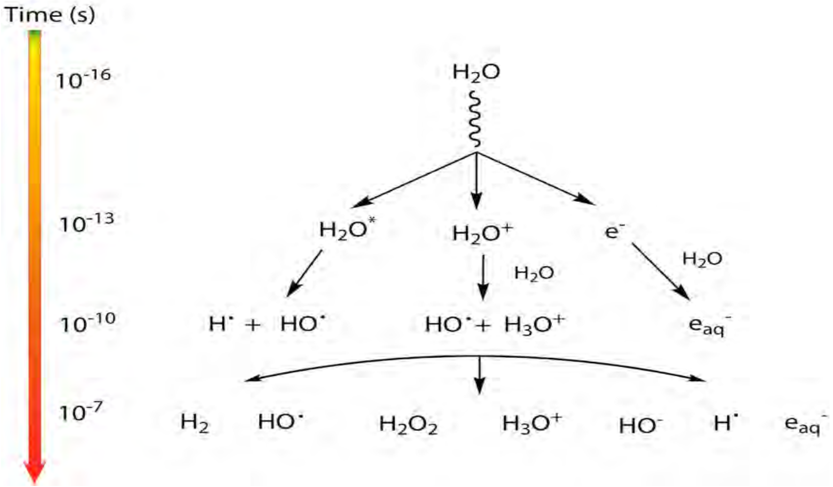

*Fig. 1. Time scale of events in water radiolysis leading to the primary products [1].*

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# I. Resonance Phenomena in Condenced Matter

# Synthesis and testing of biocompatible magnetic iron oxide nanoparticles by the nonlinear second-harmonic response method

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Magnetic nanoparticles (MNPs) are widely exploited in technical, environmental and biomedical areas [1]. MNPs like superparamagnetic iron oxide nanoparticles (SPIONs) are used in the diagnosis of diseases as contrast agents in magnetic resonance imaging and in the treatment of tumors, including hyperthermia and drug delivery. To obtain biocompatible MNPs with a specific size, we used the well-approved methodology of R. Massart [2]. As the result we obtained MNPs with a diameter of magnetic core about 10 nm.

To establish the magnetic nature of MNPs the prepared ferrofluid at concentration (2-0.02) mM(Fe)/l were investigated with original technique exploiting the second harmonic M2 of nonlinear magnetic response in parallel DC (H) and AC ($h_0 \sin\omega t$) magnetic fields. The DC field H was scanned back-and-forth symmetrically within ±300 Oe with the round-up cycles (0.125-4) s. AC field had sinusoidal form. The measurements of longitudinal nonlinear response of the second harmonic of magnetization show that MNPs correspond to superparamagnetic behavior of single domain particles and may be used for contrast increase in MR imaging of tumors (Fig. 1).

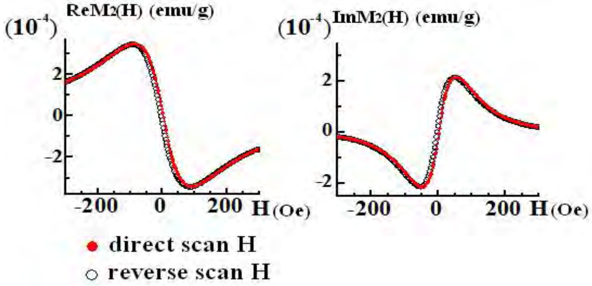

*Fig. 1. The longitudinal nonlinear response of the second-harmonic of magnetization at [Fe]=0.02 mM/l. Magnetic field scan frequency - 8 Hz.*

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# NMR in bismuth chalcogenides

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Nowadays the bismuth chalcogenides compounds like $Bi_2X_3$ where X is the tellurium or selenium ion are of great interest since they belong to a recently discovered family of three dimensional (3D) topological insulators (TIs) [1]. Despite the great number of experimental studies of these materials right after their detection, there are only few investigations of 3D TIs with nuclear magnetic resonance (NMR) until now. This lack of NMR studies is related to difficulty of getting sufficiently good signals in such crystals. 3D TIs are considered as candidates for using in magneto- and optoelectronics, spintronics and for creation quantum computers. It makes an understanding of the electron-nuclear interaction in these materials to be of particular importance. This information can be obtained by NMR.

We present results of NMR studies of the $Bi_2Te_3$ and $Bi_2Se_3$ high quality TIs. The samples were prepared in the shape of single-crystalline plates and crystalline powders. The crystallographic $\boldsymbol{c}$ axis of the single-crystalline plates was oriented during measurements parallel and perpendicular to the external magnetic field $\boldsymbol{B}_0$. The temperature range was from 11 to 293 K. NMR measurements were carried out using a Bruker Avance 400 pulse NMR spectrometer at the magnetic field 9.4 T in the Center for Diagnostics of Functional Materials for Medicine, Pharmacology and Nanoelectronics, Research park of St. Petersburg State University.

The $^{125}Te$ and $^{77}Se$ NMR spectra consisted of two lines for the all samples studied at different temperatures. These lines were associated with two crystallographically nonequivalent positions of chalcogen atoms in the structure of $Bi_2X_3$. It was found that the temperature dependence of the Knight shift for the $Bi_2Te_3$ single-crystalline plate when $\boldsymbol{c} \perp \boldsymbol{B}_0$ and powder is well described by the activation law with the activation energy 26 meV. We discovered the nontrivial behavior of the NMR spectra for the $Bi_2Te_3$ and $Bi_2Se_3$ single-crystalline plates in the orientation $\boldsymbol{c} \parallel \boldsymbol{B}_0$ at low temperatures which could not be caused by the orientational dependency in magnetic field. The phenomenon observed does not fit the theoretical models developed until now.

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# Translational diffusion and molecular mobility in series of ionic liquids based on imidazolium cations

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Ionic liquids (ILs) are ionic compounds that have a melting point below 100°C. Since the physical and chemical properties of ILs can be adjusted to the requirements of each task by careful selection of cations and anions, ILs have become widely used in many scientific studies and industrial applications [1, 2].

This study is devoted to the investigation of translational diffusion in ionic liquids based on the BMIM (butyl-methyl-imidazolium) cation with 7 variants of anions ($Cl^-$, $Br^-$, $I^-$, $BF_4^-$, $TfO^-$, $NO_3^-$, $Ac^-$) in a wide temperature range (0-75°C) using NMR methods (high resolution NMR and NMR with a bipolar pulse field gradient (bpSTE)). The measurements were carried out on the basis of the St. Petersburg State University resource center "Center for Magnetic Resonance". To reveal the influence of the fraction of water presented in all samples due to the hygroscopicity of the ionic liquids on the diffusion movement, a special drying facility was made. Two series of samples were studied: dehydrated and with controlled water content. Fig. 1 shows the temperature dependences of the self-diffusion coefficients for a series of samples with different anions before dehydration.

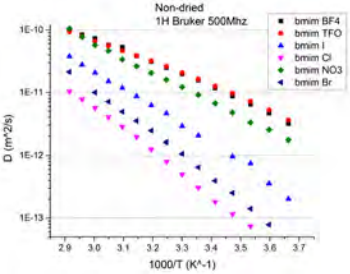

*Fig. 1. Temperature dependence of the self-diffusion coefficients for a series of samples with different anions before dehydration.*

The work is supported by the RFFI grant 17-03-00057.

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# Comparative MRI study of magnetic labelled mesenchymal stem cells and its modelled cellulose microbeads in phantom samples

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The method of magnetic resonance imaging (MRI) is widely used because of its application in medical monitoring and diagnostics. For instance, recently it was proposed to use MRI for detection and tracking mesenchymal stem cells (MSC) [1, 2]. MSC are widely used for immunotherapy in the regenerative medicine. Research of improvement of such therapy is focusing on the consideration of suitable contrast agents, particularly, superparamagnetic iron oxide nanoparticles (SPIONs), for tracking transplanted MSC by noninvasive MRI. Using of such nanoparticles for stem cell labeling makes the therapy more successful because SPIONs allow to visualize and identify location and distribution of stem cells. The magnetic labelled cells increase the contrast of MR images due to strong magnetic gradients induced by incorporated magnetic particles.

It is assumed that cellulose microbeads (CM) loaded with SPIONs potentially may serve as a good model for MRI study of MSC [3].Therefore, it seems interesting to compare CM/SPION and MSC/SPION systems.

The aim of this work is to study the influence of each system on the contrast enhancement in MR images.

The phantom samples were prepared in a 5 and 10 mm glass tube containing CM/SPION or MSC/SPION systems in agarose. MR images were recorded using Bruker Avance III 400 WB spectrometer.

- MR images of gel samples demonstrate the contrast efficiency of magnetic CM and MSC as negative contrast agents.
- CM and MSC magnetic systems provide strong shortage of transverse relaxation times $T_2$ of water protons.

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# Accounting monomers, dimers, etc. in calculating of the aggregation number in water solution of [$C_8$mim$^+$][Cl$^-$] ionic liquid

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Ionic liguids (IL), which actually are salts with melting point lower 100 Celsius degrees, are a highly interesting class of substance which is not completely investigated.

IL has a great set of significant properties, one of which is an ability to form aggregates (clusters) in aqueous solution, when the concentration of IL exceeds critical micelle concentration (CMC) [1].

An investigated system is a solution 1-octyl-3-methyl-imidazolium chloride [$C_8$mim$^+$][Cl$^-$] in water. This molecular system was studied in earlier works [2, 3] where was obtained distributions of aggregates by aggregation number. The similar researches were carried out according to other publications, for instance [4]. However, the distributions do not include monomers, dimers, etc., so called N-mers, which might be used for comparing the results to some theoretical models.

This work proposes an easy way to account the N-mers with improved algorithm as compared with [3]. The new algorithm also was rebuilt so that its speed has been increased in case of huge size of the system. As a result was obtained the more completed distribution.

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# Molecular dynamics simulation study of imidazolium-based ionic liquids – water mixtures

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Imidazolium-based ionic liquids – water mixtures have been extensively studied in the recent years for both fundamental and technological reasons. Nevertheless, the details of the structural arrangement of water molecules inside such mixtures still remain unclear. In the present study molecular dynamics simulations were employed to investigate the interaction of water molecules with ions in 1-butyl-3-methylimidazolium nitrate, iodide, and tetrafluoroborate.

Two mixtures (50 and 80 mol% of water) were studied. Simulations were carried out using the MDynaMix package [1]. Two different water models: three-site SPC/E [2] and five-site TIP5P [3], were employed. The ionic liquid ions were modeled using the potentials described in the Refs. [4-7]. Every system was simulated in the NPT ensemble at 298 K and atmospheric pressure. The effect of 1-butyl-3-methylimidazolium-based ionic liquids ions on water structural and dynamical properties were studied in details. A special attention was given to the state of water locally situated in ionic liquids.

This work was supported by the Russian Foundation for Basic Research (grant 17-03-00057a).

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# PIMD simulations of geometric and spectroscopic fluctuations of phosphinic acids monomers in vacuum

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The molecules containing proton donating and proton accepting groups are capable of forming hydrogen bonded complexes. Several examples of such molecules is given by phosphines, phosphine oxides, phosphinic and phosphoric acids, in which $^{31}$P is located quite close to the hydrogen bridge which makes this nucleus a potentially valuable probe for studying geometry and energy of hydrogen bond.

The results of our previous work [1, 2] indicate that $\delta^{31}$P is sensitive to the hydrogen bonds formed by P=O and POH groups. The formation of intermolecular hydrogen bonds alters the resulting value of $\delta^{31}$P. Therefore, in this work we focus on the study of nuclear magnetic resonance (NMR) distribution of $\delta^{31}$P in phosphinic acids monomers (Fig. 1) in vacuum. The study was conducted by means of path integral molecular dynamics simulations (PIMD). Analysis of PIMD trajectory and $\delta^{31}$P distributions allowed us to find out the most important geometric and dynamic parameters that determine the average value of $\delta^{31}$P.

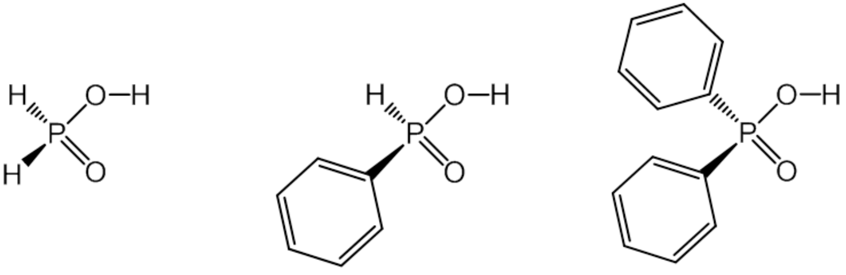

*Fig. 1. Structures of the studied model phosphinic acids.*

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# Impact of the copper-to-proton exchange on the regularity of the mordenite framework

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Copper-containing zeolites have unique magnetic, optical, electrical and other properties which make them useful for a wide range of industries. One of their application is the using them for removal of nitrogen oxides from exhaust gases (de-NO*x* catalysts) [1]. Zeolites catalytic properties are governed by many factors including the valence state of copper ions, their location and coordination in the zeolite lattice, copper content and so on, which in their turn depend on the preparation method and the initial form of zeolite [2-3]. Proton mordenite form, which has stronger acid sites, is normally obtained from ammonia form by calcination at 300 °C that often results in partial destruction of the zeolite framework. Such local destructions cannot be observed by X-ray diffraction and its detection and analysis requires application methods sensible to local structure, such as Magic Angle Spinning Nuclear Magnetic Resonance (MAS NMR).

$^{27}$Al MAS NMR allow us to determine the degree and character of the zeolite framework destruction and attribute structure imperfections. Recently it has been shown by using $^{27}$Al MAS NMR that the preparation procedure of H-MOR by calcination of NH4-MOR with Si/Al = 5 leads to a significant degradation of the mordenite framework, however, the further proton-to-copper ion exchange procedure results in its partial recovering [4].

Here we focused of the study of the impact of preparation method on the “perfectness” of the mordenite lattice. We used $NH_4^+$ mordenite with Si/Al = 10 as a starting material to produce first protonic form, and after copper-exchange form. For the copper exchange procedure two different methods were applied: microwave (MW) assisted and conventional; for deeper copper exchange the procedure repeated up to 6 times. The $^{27}$Al MAS NMR spectral analysis evidence the partial destruction of the framework of the proton form and its recovering after copper exchange. It was found that the impact of the copper exchange method on the regularity of the mordenite framework is different: MW assisted method leads to further accumulation of the defects, whereas the conventional one helps for the framework recovering.

The studies were carried out at the Centre for Magnetic Resonance of Saint-Petersburg State University. The work was funded by RFBR and CITMA according to the research project No18-53-34004.

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# The protein aggregation investigated by NMR spectroscopy and dynamic light scattering: case study of RRM2 domain of TDP-43 and SH2 domain of Fyn kinase

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Many age-related diseases, mainly in tissues with low regenerative capacity (brain, heart, kidneys), are associated with the existence of protein aggregates. It is often postulated that an imbalance of protein homeostasis is the key to the chronological aging of many cell types, and also leads to an earlier manifestation of neurodegeneration, amyloidosis, and other similar diseases in the case of genetic mutations. While biological molecules can be degraded in several ways, the presence of aggregates in biopharmaceutical preparations remains one of the main issues of quality and safety of drugs. Of even greater concern is the fact that numerous studies have shown the presence of an undesirable and/or potentially dangerous immune response in a recipient when protein aggregates are present in drugs intended for parenteral administration.

The literature describes a large number of studies of protein aggregation using observation of macroscopic and microscopic characteristics of solutions [1], as well as tracking the behavior of solvent [2] and protein molecules [3]. However, descriptions of the overall consistent picture of interactions, structural and dynamic parameters of the system with protein aggregation do not yet exist. Present study is one of the steps toward this direction.

Here we present results of study of RRM2 domain of TDP-43 protein and SH2 domain of Fyn kinase by NMR spectroscopy, dynamic light scattering (DLS) and other complementary physico-chemical techniques. The $^{1}$H,$^{15}$N HSQC spectra and DLS scans were recorded during the process of protein aggregation initiated by introduction of oxidative conditions. Thus we were able to monitor monomer fraction, aggregate sizes, kinetics and other metrics of aggregation process. It was found that the aggregation process in these systems occurs through different mechanisms: aggregates of RRM2 domain of TDP-43 protein are formed from unfolded chains, while aggregates of Fyn SH2 domain comprise folded globules.

Research was supported by RFBR grant 18-53-34003.

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# Computing small-angle X-ray scattering profiles of two-domain protein solutions from molecular dynamics simulations data

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Small-angle x-ray scattering (SAXS) is an experimental technique that is widely used to study the structure of protein solutions. However, SAXS faces some difficulties in relative positioning of protein domains in solutions of multi-domain proteins with significant domain mobility. In this case the combination of experiment and molecular dynamics (MD) simulations allows one to obtain additional information about solution structure. In particular, a shape of protein molecule can be effectively described using a so-called "pair distance distribution functions" (PDDF). This is a histogram of distances which can be found inside the molecule and can be easily calculated from MD data. The corresponding SAXS profile is a Fourier-transform of PDDF (see Fig. 1).

*Fig.1. Protein structure (left panel), corresponding PDDF (central panel) and SAXS profile (right panel).*

In the present study the aqueous solution of the two-domain Pax-5 protein (PDB code 1MDM) was chosen as test system. MD simulations were performed in a NPT ensemble (298 K and 1 atm) using the Amber14 package [1] with ff14SB force field. A single Pax-5 molecule was centered in the truncated octahedron and the rest of the cell was filled with the TIP3P water [2]. The equilibration time was 1 ns, simulation run - 1 μs. A special attention was given to the effect of protein domains dynamics on the peculiarities of calculated SAXS profiles.

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# NMR study of the Micelle Formation in the Mixture SLS-DTAB-Water

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It is well-known that the $^1$H and $^{13}$C NMR spectra of amides may show two different signals for each of the nuclei. This can be observed if the rotation about the amide bond is slow compared to the NMR time scale, and it is due to the fact that a trans-isomer nucleus is magnetically nonequivalent to the cis-isomer nucleus. Sodium lauroyl sarcosine (SLS) is an amino acid-based surfactant. The aim of this research was to study the influence of the cationic surfactant DTAB on the aggregation behavior of sodium lauroyl sarcosine at different concentration and/or variation of surfactant mole fraction.

In SLS $^{13}$C spectrum two signals from the hydrophobic tail of the molecule were observed, namely, from 9 and 10 segments at certain ratios of the content of both surfactant in the solution. This may mean that the micelle has a vesicular-like shape, i. e. when the "trapped layer" of molecules exists. A similar effect was observed earlier in SLS solutions, however at higher concentrations [1].

We believe that, at certain ratios of the concentrations of the solid and aoal, the formation of mixed micelles with two different molecular states is possible.

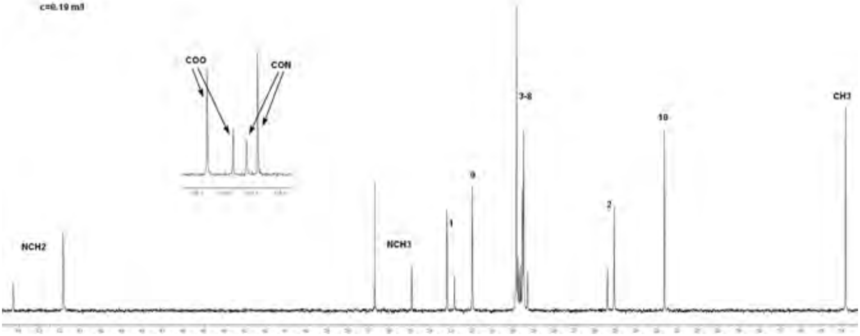

*Fig. 1. $^{13}$C NMR (b) spectra of SLS in $D_2O$ at 20 °C.*

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# Diffusion weighted imaging in very low magnetic field through stimulated echo

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The special feature of magnetic resonance imaging (MRI) is a possibility to visualize varies characteristics of investigated object. Among others a peculiar interest represents a mapping of spatial distribution of self-diffusion coefficient. A high water content in the human organism permits to use this ability as diagnostic technique in medicine. Diffusion weighted imaging is rather new effective versions of MRI.

The conventional method for obtaining diffusion-weighted images is based on the Hahn spin-echo method. But if the time of spin-spin relaxation is short, and self-diffusion is slow, then it is impossible to use the above method: the echo signal fades away before self-diffusion is manifested. This difficulty can be circumvented by applying the three-pulse method if the spin-lattice relaxation time is noticeably longer than the spin-spin relaxation time. This situation often occurs in biological objects.

The statement of the problem is connected with the fact that, despite the presence of publications at the request of a three-pulse sequence for obtaining diffusion-weighted images [1, 2], a detailed quantitative analysis of the behavior of nuclear magnetization under influence of 3 radiofrequency pulses in the presence of frequency-coding gradients and gradients for the registration of self-diffusion is absent.

In this message the results of suchlike analysis and data of an experiment on obtaining of diffusion weighted imaging using stimulated echo are presented. The experiment was made at magnetic field 7 mT using the laboratory homebuilt nuclear magnetic resonance imager in department of Nuclear-Physical Research Methods. For realization of the imaging pulse sequence the special program was created in the LabVIEW environment.

As way of "fantoms" was used samples of agarose gel doped with $MnSO_4$ solution. In this way it was possible to obtain samples with lent diffusion and different spin-spin and spin-relaxation times.

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# S. First Steps in Science

# Theoretical and Experimental Study of Electronic Structure and Excited-State Dynamics of copper(II) Chloride Complexes in Dichloromethane

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In this work, the electronic spectra of individual copper(II) chloride complexes ($CuCl^+$, $CuCl_2$, $CuCl_3^-$, $CuCl_4^{2-}$) and their stability constants in dichloromethane were determined using steady state absorption spectroscopy. Obtained values of stability constants in dichloromethane are significantly larger than that in solvents with some donor ability. The geometries of copper(II) chloride complexes were optimized and vertical excitation transition (VET) energies were calculated at the DFT and TD-DFT levels of theory, respectively. The obtained VET energies are in agreement with the experimental electronic spectra of individual copper(II) chloride complexes.

The excited-state dynamics of $CuCl_4^{2-}$ complex in dichloromethane was studied using ultrafast transient absorption spectroscopy upon excitation into all possible d-d or Ligand Field (LF) electronic states, and three most intense Ligand-to-Metal Charge Transfer (LMCT) electronic states. The LF states are found to be nonreactive states, while excitation into the LMCT states leads to the ionic dissociation of $CuCl_4^{2-}$ complex followed by the recombination into parent complex. The lifetimes of LF excited states were determined to be of < 200 fs ($^2E$), ≈ 1 ps ($^2B_1$), and ≈ 5.5 ps ($^2A_1$). The large difference in lifetimes was explained from theoretical point of view by Time-Dependent Density Functional Theory (TD-DFT) calculations. The intersection between $^2B_2$ ground state and $^2E$ LF excited state was discovered, whereas $^2B_1$ and $^2A_1$ LF excited states do not cross either ground electronic state or each other. The Franck-Condon mode is found to be Cl-Cu-Cl “umbrella” bending vibration.

Majority of the short-lived LMCT excited states undergo internal conversion to the lower-lying vibrationally hot LF excited states, which then either nonradiatively decay to the ground state, whereas minor number of LMCT-excited complexes undergo Cu-Cl ionic bond dissociation, forming $CuCl_3^-$ and $Cl^-$ ions, which then recombine re-forming parent complex. In case of LMCT excitation the Franck-Condon mode is ought to be asymmetric Cl-Cu stretching vibration.

**Acknowledgments.** Calculations have been made with the assistance of the Saint-Petersburg State University Computer Center. Optical measurements were performed at the Center for optical and laser materials research of Saint-Petersburg State University.

# Physical properties of carbon fabric

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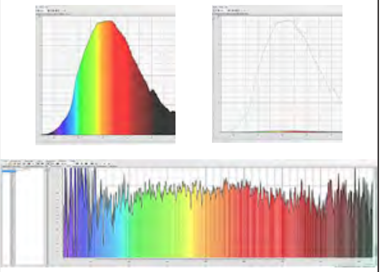
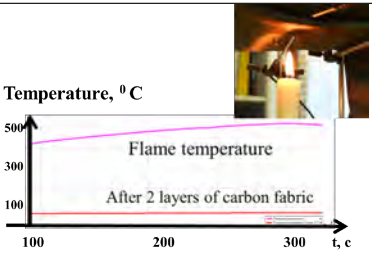
The problem of protecting of space capsule (SC) from the effects of high temperatures resulting from aerodynamic heating when SC enters the dense layers of the atmosphere is important in connection with the many-sided modern space research. Protection of SC by coatings, collapsing under the action of temperature is the most common. Lightweight and durable carbon fiber is considered the most promising material for their creation. In the work, a sample of carbon fabric provided by the company Pro Composite was investigated.

Scientific research were performed at Saint-Petersburg cadet military corps and the Research Park of St.Petersburg State University «Educational Resourse Center of Physics».

Some physical properties of carbon cloth have been investigated in various ways: carbon fiber thickness was estimated (~ 10 μm); experimentally demonstrated strength of carbon fabric and proved the ability of carbon fabric to absorb energy in the visible spectrum and thermal. When the sample was heated by a candle flame from 25 to 5000 ° C, it did not reflect heat, did not burn, did not smoke, and during the experiments no additional odor appeared. It was found that the use of a protective coating lowered the temperature more than 5 times. The most surprising was the fact that 1 layer of carbon fabric, seeming openwork on the lumen has the same protective effect as 4 layers.

| Sample bandwidth in the visible spectrum – 1% | Graph of temperature versus heating time |
|---|---|
|  |  |

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# The study of ionic liquids using NMR

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NMR is one of the most useful and informative methods in exploration of substances. Benefits of using this technology might be showeт with an example of ionic liquid. Method of NMR-diffusometry is a straight way to define self-diffusion coefficient. Therefore the purpose of our study is identification self-diffusion coefficient by using NMR-diffusometry and its temperature dependence. The object of our study is ionic liquid, 1-Butyl-3-methylimidazolium.

Hypothesis: coefficient of self-diffusion increases with increasing temperature.

Problems:

1. Register pseudo two-dimensional spectra of ionic liquid in spectrometer Bruker Avance 500 Mhz.
2. Get the useful spectra from set of FID by using software MestRenova ,MagicFlot based on Fourier transform.
3. Define self-diffusion coefficient of ionic liquid with different temperatures. Create the graph of its temperature dependence.

As a result of work spectra of ionic liquid were obtained, they were processed and analyzed by using software MestRenova, MagicFlot.

With the help of these programmes self-diffusion coefficient and its temperature dependence were defined.

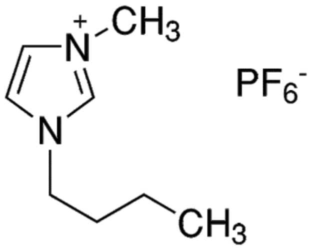

*Fig. 1 Ionic liquids 1-Butyl-3-methylimidazolium.*

**Acknowledgements**: The NMR measurements have been carried out in Center for Magnetic Resonance of Research Park of St. Petersburg State University.

# The Research of Nematic Liquid Crystals

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The relevance of the study of nematic liquid crystals is due to their widespread use in the modern world. The arrangement of molecules in liquid crystals changes under the influence of various factors which leads to a change in their optical properties. This allows to use liquid crystals in various technical areas, for example, in the displays of various devices such as phones, computers, tablets, etc.

In the course of the work, an experimental cell, which consisted of two plane-parallel glass plates with current conductive layers, was used. A liquid crystal was placed between the plates. Voltage from the generator of electrical signals was applied to the conductive coatings. As a result, experimental curves of light transmission depending on the voltage and angle of incidence were obtained.

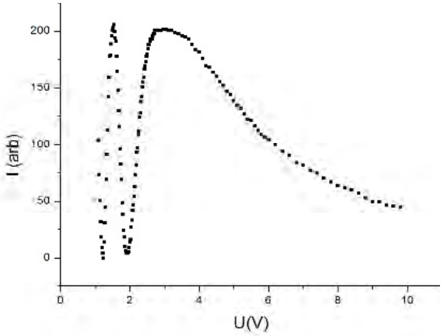

*Fig. 1.Dependence of light transmission on voltage.*

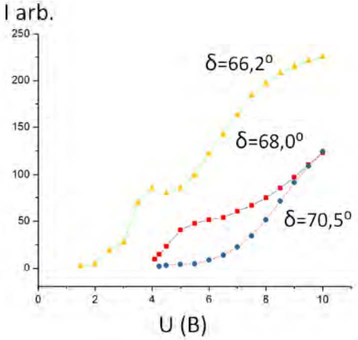

*Fig. 2. Dependence of light transmission on voltage and angle.*

The Research of Nematic Liquid Crystals has been carried out in Research Park of St. Petersburg State University.

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# Теоретическое моделирование отражательной способности многослойных зеркал для изучения короны Солнца

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Мягкое рентгеновское излучение (длины волн от 1 нм до 40 нм) при отражении от поверхности любого материала имеет малый коэффициент отражения (от одной сотой до нескольких процентов) при нормальном падении. При использовании малых углов скольжения коэффициент отражения приближается к значению в 100%, однако при этом в значительной степени увеличиваются аберрации, затрудняющие фокусировку излучения. Для обеспечения применения оптики нормального падения с большим коэффициентом отражения мягкого рентгеновского излучения применяются многослойные зеркала (МЗ): периодические структуры, состоящие из тонких слоев сильно- и слабо-поглощающих материалов, соответственно, нанесенных на атомарно гладкую поверхность подложки. МЗ имеют широкое применение: литография, микроскопия, рентгенофлуоресцентный анализ, коллимирующая и изображающая оптика и др.

В данной работе проводился теоретический расчет МЗ, применительно к исследованиям короны Солнца. Излучение короны в основном приходится на далёкий ультрафиолетовый и рентгеновский диапазоны, не пропускаемые земной атмосферой, поэтому очень большое значение имеет изучение солнечной короны с помощью космических аппаратов. Применение МЗ в космических телескопах позволяет получать четкое изображение короны Солнца в строго определенном «цвете» - на отдельной спектральной линии, что необходимо для изучения структуры и распределения температуры в короне Солнца.

Целью данной работы являлось определение оптимальных пар материалов для изучения спектральных линий излучения ионов короны Солнца *FeIX-FeX* ($\lambda$=12.5 нм), *HeII* ($\lambda$=17.1 нм) и *FeXXI* ($\lambda$=30.4 нм) и оптимизация параметров МЗ: период ($d$), отношение толщины сильнопоглощающего слоя к периоду ($\gamma$) и число пар слоев ($N$) для достижения наибольшего коэффициента отражения и наименьшей ширины брэгговского пика многослойного зеркала.

# Определение состава и каталитической активности соединений вида $[Ln(en)_x][Fe(CN)_6]$

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Смешанные оксидные системы могут выступать катализаторами в самых разнообразных химических реакциях. Термическое разложение двойных комплексных солей (ДКС) в атмосфере воздуха является одним из наиболее удобных способов получения смешанных оксидов. Основным преимуществом этого метода является строгая стехиометричность полученного оксида, так как соотношение количеств металлов четко задается структурой соли.

Данная работа посвящена исследованию соединений типа $[Ln(en)_x][Fe(CN)_6]$ (Ln = La, Gd, en = 1,2-диаминоэтан). В рамках представленной работы проводится количественное определение соотношения количеств металла и этилендиамина в составе соединения, а также изучение каталитической активности оксидов состава $LnFeO_3$, образующихся при прокаливании исходных ДКС в атмосфере воздуха при 800°C на примере реакции разложения перекиси водорода.

# Беспилотное транспортное средство

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По статистике [1], только в прошлом году в России произошло более 160000 ДТП. В значительном числе случаев аварии удалось бы избежать, если водителя заменил бы автопилот. Наиболее оптимальным решением является создание беспилотного транспорта, который бы позволил снизить количество ДТП. Такие компании, как Google, Яндекс, Uber и Tesla, активно ведут разработку беспилотных автомобилей.

Для лучшего понимания того, с какими проблемами сталкиваются инженеры при разработке своих решений наша команда поставила себе целью создать прототип беспилотного автомобиля.

Основой нашего решения стала разработка программного обеспечения, позволяющего принять решение с низкой вероятностью ошибки при детектировании и классификации объектов на дороге. В перспективе дальнейшего развития будет добавлено использование сонаров, лидаров, большего количества камер, а так же алгоритм будет представлять из себя нейронную сеть.

Практическое использование автопилота позволит в перспективе снизить количество ДТП на дорогах, сохранять жизни и здоровье людей, повысить конкурентоспособность российских автопроизводителей и снизить стоимость перевозки пассажиров.

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# Экспериментальное изучение влияния тонких барьерных слоев на рабочие параметры многослойных зеркал

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Изучение спектров коротковолнового электромагнитного излучения, например, мягкого рентгеновского излучения (МРИ), а также создание оптической техники для данного диапазона длин волн является нетривиальной задачей в виду того, что МРИ активно взаимодействует с веществом: интенсивность МРИ при проникновении в вещество ослабляется в *e* раз уже на глубине в доли микрометра. Также важно, что в случае классических (массивных) зеркал МРИ отражается только при малых скользящих углах – в зоне полного внешнего отражения (ПВО). Однако в ряде приложений (солнечная астрономия, рентгеновская литография и др.) такая геометрия отражения неприемлема, а при углах падения, близких к нормали, коэффициент отражения МРИ от классических зеркал крайне низок.

Напротив, многослойные периодические зеркала (МЗ) обладают высоким коэффициентом отражения при практически нормальном падении МРИ (в определенном узком диапазоне длин волн) благодаря конструктивной интерференции МРИ, отраженного от каждой границы раздела соседних слоев. При этом необходимо, чтобы оптические постоянные материалов пары слоев сильно различались, а границы раздела были максимально резкими. Однако, при производстве МЗ неизбежно происходит взаимодиффузия и химическое взаимодействие материалов соседних слоев, а их поверхность обладает шероховатостью, что все вместе формирует протяженную межфазовую границу и приводит к значительному ухудшению отражательной способности МЗ. Возможным решением этой проблемы может стать внедрение в периодическую структуру зеркала определенных барьерных слоев, которые должны уменьшить протяженность межфазовых границ.

Целью работы была экспериментальная проверка влияния барьерных слоев $B_4C$ и Be на отражательную способность Mo/Si МЗ. На рентгеновском спектрометре РСМ-500 были получены кривые отражения МЗ с и без барьерных слоев. Было подтверждено, что введение барьерных слоев улучшает отражательную способность МЗ на 9,3%. Далее с помощью теоретического моделирования экспериментальных кривых отражения (в программе IMD 5.04) было доказано, что введение барьерных слоев уменьшило протяженность межфазовых границ на 0,6-0,9 нм.

# Crystallization of Rose's metal at different temperatures

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Technologies based on crystallization of molten metals like molding, forging and quenching play a major role in advancement of human civilization. The parameters of crystallization's process of melt define the metal's structure, its mechanical and electrophysical characteristics, which are important for engineering of the materials for high technology applications.

The goal of our project was to research of the structure of Rose's metal crystallized at different temperatures. We have investigated the phase composition of samples of Rose's metal and size distribution of metal grains.

Sample preparation procedure had several steps. Firstly, we melted small pieces (about 3-4 mg) of Rose's metal with electric stove and froze them by casting on metal plate. The temperature of metal plate varied from -196°C to 90°C. Then samples were investigated with scanning electron microscope (SEM), and afterwards were etched in 3% HNO3 solution in ethanol to make metal grains more visible and were investigated with SEM again.

All samples had metal grains (Fig. 1). Grain sizes varied from 0,21 µm to 22 µm with mean value of about 1 µm and had two kinds: with higher tin content (70% Sn, 20% Bi, 10% Pb) and with lower tin content (50% Bi, 30% Pb, 20% Sn). There were both small grains with mean size about 1 µm and huge grains with mean size 5 µm at high temperatures. There were only small grains at low temperatures.

We have demonstrated that metal structure depends on temperature of medium at the moment of crystallization. The possible explanation of this effect is dependence of nucleation rate and crystal growth rate on overcooling of melted metal.

*Fig. 1. SEM image of the surface of sample. Dark grains contain more tin, light - more bismuth.*

# Изготовление действующих моделей часов. Механические часы: свойства и особенности их работы

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В нашей повседневной жизни мы так часто пользуемся временем, что даже не задумываемся и не подозреваем, что же это такое? Дать ответ на этот вопрос нелегко. В самом общем виде можно сказать, что время – это непрерывная череда сменяющих друг друга явлений. Главное свойство времени состоит в том, что оно длится, течет безостановочно. Пространство можно оградить, но время остановить невозможно.

В модели часов мы исходили из расчёта, что длина маятника будет составлять примерно 25 – 30 см. Период собственных колебаний такого маятника сможет обеспечить бесперебойную работу данного механизма.

Маятниковые часы, даже заводского изготовления, при запуске очень требовательны к ориентации корпуса часов относительно отвесной линии. В нашей модели пластмассовые шестерёнки, «проявили» хорошие качества, такие как лёгкость на раскручивание; достаточная жёсткость для передачи вращения; удобство в сборке; низкая стоимость.

В нашем случае, когда точность присадки всех отверстий под оси для шестерёнок определяется человеческим фактором, требования к ориентации часов по отвесной линии соблюсти ещё труднее…

Конструируя механические часы, мы постоянно возвращались к мысли, связанной с измерением времени при помощи других конструкций часов, например, песочных. Происхождение песочных часов уходит далеко вглубь веков. Они состоят из двух стеклянных колб, одна поверх другой с узким отверстием между ними. Песок постепенно попадает из верхней части в нижнюю часть при переворачивании часов. Когда весь песок из верхней части перешел в нижнюю часть, то это означает, что время вышло, однако, это не всегда означает, что прошел час.

Мы решили их модифицировать и сделать их плоскими и повесить на стену. Однако, через некоторое время часы работать переставали, так как песок не попадал из верхнего сосуда в нижний. Причины плохой сыпучести песка в нашей модели мы сможем определить и устранить их при дальнейших исследованиях.

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# Экспериментальное исследование дифракции на щели в воздухе и в воде

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Дифракция волн - явление отклонения от прямолинейного распространения. Дифракция тесно связана с интерференцией. В данной работе мы экспериментально исследовали дифракцию ультразвука с частотой 40 кГц в воздухе и с частотой 80 кГц в воде. Были построены графики зависимости амплитуды ультразвуковых волн от угла наблюдения для волн в воздухе и от поперечной координаты для волн в воде. Для измерений в воздухе использовали стандартный гониометр фирмы PHYWE, измерения проводились в Научном парке СПбГУ. Измерения в воде проводились в гидроакустическом бассейне кафедры радиофизики. Сравнение экспериментальных данных с расчётными показало качественные совпадения.

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# Исследование источников света с помощью спектрального анализа

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Актуальность нашего исследования заключается в том, что изучение спектрального анализа различных источников света и его методов востребовано в связи с его широким применением в повседневной жизни и в разных отраслях науки. Данная работа проведена с использованием оборудования ресурсного центра Научного Парка СПбГУ «Ресурсный образовательный центр по направлению Физика». Нами было произведено несколько экспериментов. Первый из них исследование спектральных характеристик источников света различного типа.

Было проведены измерения коэффициента пульсации освещенности. Измерение коэффициента пульсации освещенности производилось при помощи осциллографа и фотоприемника.

Результаты эксперимента представлены в таблице.

| Лампа | Emax(B) | Emin(B) | Кп(%) |
|---|---|---|---|
| Энергосберегающая | 4 | 3.3 | 9.6 |
| Накаливания | 6.4 | 5.2 | 10.3 |
| Ртутная | 6.6 | 2 | 53.4 |
| Галогенная | 2.05 | 1.55 | 13.9 |
| Светодиодная | 0.29 | 0.27 | 3.6 |

Из этого эксперимента можно сделать вывод, что светодиодная лампа лучше всего воспринимается глазом, так как воспринимается как постоянный свет. Ртутная лампа имеет наибольший коэффициент пульсации. С таким коэффициентом пульсации источник света можно использовать только в местах временного пребывания.

Вторым экспериментом стало исследование зависимость спектрального состава излучения различных светодиодов от величины тока питания.

В ходе эксперимента было установлено, что максимум у синего, зелёного, белого, красного и жёлтого светодиодов смещается в длинноволновую область при увеличении силы тока питания спектры различных источников света, мы смогли определить наиболее подходящие для той или иной области применения. Выявили достоинства и недостатки того или иного искусственного источника света. А также определили зависимость спектрального состава от силы тока питания у светодиодов.

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# Исследование возможностей повышения КПД двигателя Стирлинга

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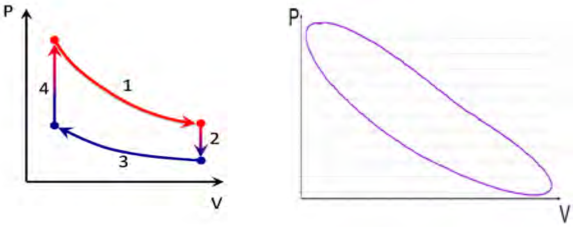
В процессе работы мы сделали практические измерения характеристик двигателя Стирлинга в его лабораторной версии. Данная работа проведена с использованием оборудования ресурсного центра Научного Парка СПбГУ «Ресурсный образовательный центр по направлению Физика».



(а) (б)

*Рис.1. График цикла Стирлинга: а) идеальный, б) реальный*

С помощью датчика нагрузки мы измерили момент силы (также крутящий момент, вращающий момент) работающего двигателя. Среднее значение КПД без кожуха примерно равно 0,089.

В нашем распоряжении оказалась модель двигателя с кожухом, который не подходил по своим параметрам к данному двигателю. Пламя не оставалось ровном положении, а постоянно «двигалось». Был изготовлен кожух из жестяной банки. Сделанный нами кожух смог оградить пламя от посторонних вмешательств, увеличив температуру в области нагревания (Тн). После чего было установлено, что изменилась температура запуска двигателя Стирлинга - она уменьшилась с 60 °С до 50 °С. Рассчитав те же физические величины уже с кожухом, выяснили, что и механическая энергия (Wm), и энергия трения (Wtr) увеличились. Увеличился также и КПД до 0,156. Одновременно мы высчитали КПД$_{max}$, чтобы оценить насколько близок предел повышения КПД двигателя в данных условиях.

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# Исследование основных характеристик современных источников освещения

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В ходе выполнения данной работы были изучены технико-экономические характеристики различных источников света. Результаты представлены в виде таблицы; КПД, срок службы, стоимость службы в расчёте на 1000 часов и цена лампочки (таблица 1).

*Таблица 1. Основные характеристики современных источников освещения.*

| Вид лампы | **КПД** | Срок службы | Стоимость службы | Цена лампочки |
|---|---|---|---|---|
| Лампа накаливания | 5% | 1000 часов | 255 р. | 24 р. |
| Люминесцентная лампа | 20% | 12000 часов | 50 р. | 140 р. |
| Светодиодная лампа | 90% | >30000 часов | 21р. | 300 р. |

Для снятия вольтамперных характеристик диодов была собрана схема, включающая в себя источник питания (генератор), амперметр, вольтметр, резистор и рассматриваемый тип светодиода. Были исследованы ВАХ для зелёного, красного, синего, жёлтого и белого светодиодов, являющихся основой светодиодной лампы.

В ходе работы были изучены строение и технические характеристики трёх источников света: лампы накаливания, люминесцентной (энергосберегающей) лампы и светодиодной лампы. Исследования показали, что наиболее перспективным, долговечным и выгодным в использовании типом лампы на данный момент является светодиодная лампа. Данная работа проведена с использованием оборудования ресурсного центра Научного Парка СПбГУ «Ресурсный образовательный центр по направлению Физика».

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# Synthesis and Application of Metallic Nanoclusters

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Recent advances of nanotechnology have produced a fundamentally new class of fluorescent labels named metallic nanoclusters (NCs). Due to their unique physical and chemical properties, NCs occupy a middle position between individual atoms and nanoparticles and can be applied in various fields of science: medicine, microbiology, chemistry. Singlet oxygen which is generated during luminescence may be used in photochemotherapy to fight cancer. Investigating of metal nanoclusters is young but promising area for research.

Spectrofluorimetry, microscopy and spectrophotometry were the main methods used to study silver and gold nanoclusters synthesized on BSA (bovine serum albumin). Fluorescence emission/excitation and absorption spectra of the nanocluster's were recorded and analyzed. Synthesized nanoclusters were implanted in yeast cells. The success of the experiment was also confirmed on a luminescent microscope. We even could watch cell organelles.

Nanoclusters can be synthesized on different organic bases (e.g. on natural DNA, oligonucleotides, proteins or amino acids, etc). In this research we used BSA but we are going to try other matrixes in the future.

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# Исследование применения углеродных нанотрубок для очистки питьевой воды

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При очистке больших объемов применяется ряд физических методов, способных проводить глубокую очистку воды, но, как правило, производительность таких методов мала.

Эффективность работы мембранных систем во многом определяется используемыми для их изготовления материалами. Внедрение наноматериалов в структуру мембран создает возможности повышения проницаемости, устойчивости против загрязнения, повышает механическую и термическую стабильность, а также обеспечивает приобретение новых свойств мембран.

В ходе исследования мы рассматривали актуальный для современного человека вопрос, который касается возможностей очистки воды с применением нанотехнологий. Высокой эффективностью обладают фильтрующие среды на основе углеродных нанотрубок. При подводе небольшого импульсного напряжения (2-3 В) к многостенным углеродным нанотрубкам уничтожение задержанных бактерий и вирусов происходит за несколько секунд с минимальными энергозатратами.

Нанесение покрытий, содержащих наноматериалы, на внутреннюю поверхность емкостей и трубопроводов препятствует образованию биопленок и развитию коррозии. Другим перспективным направлением считают использование наноматериалов для уменьшения биозагрязнения фильтрационных мембран. Внедрение противомикробных и фотоактивных материалов на основе нанотехнологий позволяет использовать мембраны не только в качестве физического барьера, но придать им свойство "реагирования" на состав фильтруемой среды.

Исследования были проведены в лабораториях Университета ИТМО и Академии талантов Санкт-Петербурга.

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# Table of Content

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