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German-Russian
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St. Petersburg – Peterhof
October, 17-21
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Invited Lectures

Magnetism of the Heavy Lanthanides: Equilibrium vs. Non-equilibrium Phase Transitions

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What is the difference between localized and itinerant magnetic moments? How does the localization affect the magnetic phase transition? What are the roles of exchange splitting and spin polarization? The unique magnetic behavior of the heavy lanthanides provides answers to questions like these. The magnetic phases of the lanthanides range from simple ferromagnetism to exotic anti-ferromagnetic phases. Studying the transitions between these phases teaches us which microscopic interactions can lead to the different forms of magnetism.

This lecture focusses on the simplest type of these phase transitions, the ferromagnetic to paramagnetic phase transition of gadolinium occurring at room temperature. Across this transition, the exchange splitting of valence states has been found to persist even in the paramagnetic phase, when there is no macroscopic magnetic order [1].

One of the valence states showing this puzzling behavior is the d_z^2 surface state, which can be studied particularly well in spin-resolved photoelectron spectroscopy. Using this technique to study the phase transition out of equilibrium, when it is driven by laser excitation, allows us to disentangle interactions by the different timescales they occur on. Here, in contrast to the persisting exchange splitting in thermal equilibrium, the exchange splitting of the valence states is reduced quickly while a macroscopic spin polarization remains for a long time [2]. This behavior can lead back to the localized nature of the magnetic moments in gadolinium.

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Ultrafast Photochemistry of Bromoform: Chemical Reaction from the Inside

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The ultrafast photochemistry of bromoform (CHBr_3) was studied in acetonitrile and methanol using UV-vis femtosecond transient absorption spectroscopy. Upon 255-nm excitation, bromoform molecule was promoted into $n_{\text{Br}}\sigma_{\text{C-Br}}^*$ excited state resulting in C-Br bond breaking with the formation of CHBr_2 radical and bromine atom. Radical byproducts undergo geminate recombination due to the solvent cage effect within 10 ps time forming the iso-bromoform with C-Br-Br bond or escape the solvent cage. The iso-bromoform can be also formed as a result of direct excited-state isomerization in less than 100 fs. The isomer is stable in non-polar methylcyclohexane for several microseconds, but undergoes back-isomerization into the parent molecule within 250 ps in polar acetonitrile. Quantum-chemical calculations explained the solvent effect by polar nature of the transition state for the back-isomerization reaction.

In gas phase, the ultrafast photochemistry of bromoform was studied by means of UV-vis femtosecond transient absorption spectroscopy and femtosecond electron and ion covariance coulomb explosion spectroscopy. The 250- and 266-nm excitation of bromoform results in its decomposition into CHBr_2 and Br or CHBr and Br_2 as well as direct excited-state isomerization within 40 fs. The formed isomer possess the large excess of vibrational energy resulting in fast (90 fs) decomposition of the isomer into either CHBr_2 and Br or CHBr and Br_2 . Quantum-chemical calculations demonstrated the presence of conical intersection between the excited-state potential energy surface (PES) of the parent molecule and the ground-state PES of the isomer confirming the direct excited-state isomerization path. Surprisingly, using time-resolved coulomb explosion spectroscopy, the Br_2 formation by the roaming reaction mechanism from the CHBr_2 and Br radicals was discovered. Thus, the bromine atom was observed to roam around CHBr_2 byproduct for a relatively long time, about 1 ps, and then eliminate the bromine atom forming CHBr and Br_2 . The additional experiments will be performed to confirm the roaming reaction mechanism.

Acknowledgments. Authors acknowledge G-RISC for funding the visits to DESY (Hamburg, Germany) to perform the coulomb explosion experiments in the gas phase.

Label-Free Spectromicroscopy as a Probe for Dermal Drug Delivery

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Label-free approaches in spectromicroscopy permit to follow topical drug delivery with high spatial resolution combined with chemical selectivity and high sensitivity. Recent progress in this field is reported, where X-ray microscopy, stimulated Raman microscopy, and related techniques are applied. Antiinflammatory drugs are topically applied to *ex vivo* human, murine, and porcine skin samples by using drug solutions, formulations, as well as polymeric drug nanocarriers. Drug nanocarriers are used for facilitating the transport of drugs across skin barriers as well as triggered drug release. Detailed studies using X-ray microscopy are presented, allowing us to probe absolute drug concentrations penetrating human skin samples. Drug penetration processes are derived and the role of drug nanocarriers penetrating the skin barrier is determined. The experimental results are modeled by the diffusion of drugs using Fokker-Planck equation. This provides evidence for diffusion and free energy barriers controlling the drug transport.

High spatial resolution studies allow us to locate the drugs in different skin regions and help to develop a molecular understanding of dermal drug and drug carrier penetration processes. Detailed studies also focused on the role of barriers for drug penetration. Furthermore, changes in drug penetration induced by mechanical damage of the skin barrier by tape stripping as well as inflammatory skin diseases are presented.

Acknowledgments. Financial support by German Research Foundation and SFB 1112 is gratefully acknowledged.

Making Sense of the Mess: Reconstructing the Morphology of Noncrystalline Solids from NMR of Noncovalent Interactions

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Gases are formless; in an ideal gas one can neglect intermolecular interactions. Crystals are perfectly shaped; this shape is governed by intermolecular interactions. These states of matter are the starting points for an introduction to the physical properties and structure of matter. Each first-year student studying natural science is expected to be able to make a short spontaneous presentation about one of these topics. The situation is different when one is asked how to map the structure of a noncrystalline object, what interactions determine this structure, or simply, “Why rubber is elastic?”. There are many methods that can provide the chemical composition of very complex materials. There is a lack of methods suitable to study intermolecular interactions even in simple noncrystalline solids. In turn, these interactions are responsible for the mechanical and chemical properties of these solids.

Magnetic resonance spectroscopy (NMR) is the method of choice for such applications. The only critical requirement of NMR is the presence in the system of interest of spin-labels that will be suited to the problem under study. Give me a proper spin-label - and I will turn the subject matter inside out.

This presentation will cover the following aspects: (i) short introduction to NMR and specifically solid-state NMR; (ii) conventional structure elucidation using solid-state NMR [1]; (iii) the effect of noncovalent interactions on NMR parameters [2, 3]; (iii) the study of the chemical reactivity and the morphology of surfaces [4]; iv) the reconstruction of the morphology of noncrystalline inorganic and organic solids from NMR parameters; (v) time-efficient DFT calculations as a complement to solid-state NMR [3, 5].

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A. Chemistry

Catalytic Activity of Copper Nanostructures Produced by on-Line LCLD Method

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The laser-induced metal deposition technique [1] attracts a great interest not only due to its application in microelectronics and manufacturing of electrochemical sensors but also due to its possible implementation for on-line laser synthesis of nanostructured metal catalysts directly in the reaction mixture. In turn, the synthesized nano-sized metal structures may take part in organic catalysis using solvent as a reaction medium.

In this work the catalytic properties of copper nano-sized structures producing directly during laser-induced synthesis and their influence on the processes [2] which occur in solution were studied. The synthesized copper nanoparticles were tested on model and well-known reaction of organic catalysis such as reforming of ethanol. In this reaction the laser irradiation-dependent formation of ethanal, ethylene methane was observed along with release of hydrogen, water and carbon dioxide (Fig. 1).

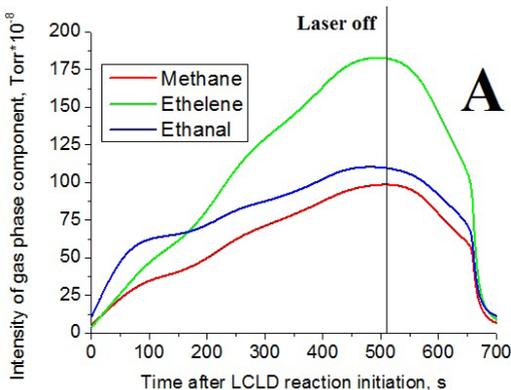


Fig. 1. B-homo analogues of steroid estrogens.

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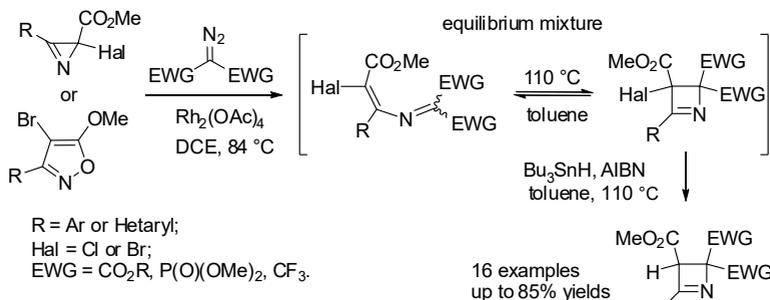
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Synthesis of Apoptosis-Inducing 2,3-Dihydroazetes

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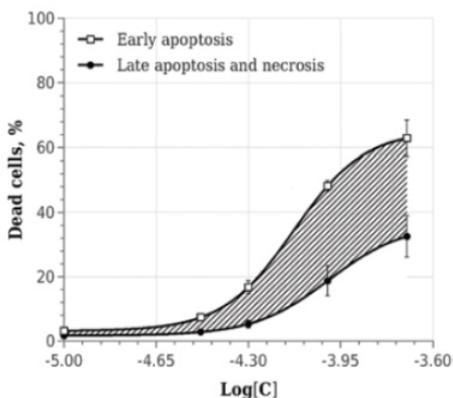
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We have developed an effective two-step method for the preparation of thermally stable and differently substituted, at the C2- and C4-positions, alkyl 2,3-dihydroazete-2,3-di-/2,2,3-tricarboxylates that can operate both with alkyl 2-halogen-azirine-2-carboxylates and 4-bromo-5-alkoxyisoxazoles as starting materials.



In vitro cytotoxicity tests on THP-1 cell line revealed that 2,3-dihydroazete-2-,3-dicarboxylates greatly differ in their ability to induce apoptosis and/or necrosis. To adequately describe and quantitatively assess the apoptosis/necrosis potential, the difference between the two areas under the curves of concentration dependency of apoptosis/necrosis induction within the concentration range is expedient. Trimethyl 4-phenyl-2-,3-dihydroazete-2,2,3-tricarboxylate has the maximal apoptotic potential coupled with high cytotoxic and minimal necrotic potential, being a good candidate for further studies of its anti-cancer activities.

Acknowledgements. The authors greatly appreciate financial support of RFBR (14-03-00187, 16-03-00596, 16-33-60130, 16-33-00651) and SPbSU (12.38.239.2014, 12.38.217.2015) grants.



Laser Induced Liquid-Phase Molybdenum Oxide Deposition

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This study presents investigation and comparison of different samples obtained by LCLD method from solutions containing molybdenum trioxide and sorbitol as reducing agent. Laser beam can be locally focused on the target surface with following deposition of very small and narrow tracks, which is useful for micro-electronic technologies. Temperature in the focus may reach up to 2000°C, at these high temperatures a lot of new and unexpected chemical reactions may take place. Study of mechanisms of these reactions opens many new opportunities for chemistry. Laser induced deposition is cheap and easy way to obtain oxides or metals from water-based solutions.

Molybdenum oxides are semiconductors, what makes them expired objects for study and usage as gas sensors. The goal of further work is to develop prototype of gas sensor, to study it's features, electrochemical properties, selectivity on different gases, and response.

Tracks of molybdenum oxides were obtained with LCLD method from different series of solutions. Special attention is dedicated to spectral properties of the water-based solutions, spectra were identified using quantum-mechanical methods, supported by literature data, often contradictory. According to data from spectra the structure of molybdenum oxide in the solution was suggested. The dynamic of oxides distribution on the tracks deposited from different solutions was studied by XPS method. Using SEM, EDX, and RFA methods identification of the composition of the tracks was made. Based on the RFA data and impedance spectroscopy the state of molybdenum in the tracks was determined.

Study of the Structural-Dynamic Characteristics of the Ternary System CsCl-LiCl-D₂O with NMR Spectroscopy in the Interval from 25° C to the Freezing Temperature

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Multicomponent aqueous electrolyte solutions are characterized by wide diversity of physical-chemical properties, thus and so the study of formation mechanisms and conditions of joint compounds in these systems is a crucial task. Variety of properties of such systems include hygroscopicity, high solubility and heat capacity, low freezing temperatures, and formation of joint compounds. The system under study is a model system, due to the different nature of the salts included: chaotropic CsCl and kosmotropic LiCl. The formation of joint compound goes by the structurally forced embedding mechanism [1].

The results of investigation of suchlike systems with NMR spectroscopy method allow one to receive a notion of nearest surrounding of the ions and of the system structure on the whole, since the NMR method is sensitive to the appearance of microheterogeneity in the solution. Discrepancy between natures of the salts reflects in their different influence on the water molecules mobility. Thus it's interesting to reveal dominant influential in the joint solution. Temperature studies NMR are suitable for the determination of dominant salt. By applying of NMR method we received ²D, ⁷Li, ¹³³Cs spin-lattice (T1) and spin-spin (T2) relaxation times (sec), shifts (ppm) for the samples with constant ratio CsCl:LiCl = 1:2, at different concentrations, we refined freezing points of these solutions, and deduced dependency of the velocity of the magnetic relaxation from the temperature at various concentrations. The temperature boundaries of microheterogeneity appearance – formation of CG (cybotactic groups - precursors of solid phase) are detected. Acquired structural-dynamic parameters for the title system are compared with the ones for the binary systems. The dominant influence of the components in the ternary system is determined.

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Langmuir-Blodgett Films Based on Nickel Stearate as New Metal Affinity Sorbents

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Chromatography is the most frequently used analytical method. a huge amount of information about the structure and properties of many classes of organic compounds was obtained by this method.

There are several types of chromatography, in particular – immobilized metal affinity chromatography (IMAC), which is based on specific interactions typical for certain biochemical processes. This is a highly specific and effective method, based on different affinities of organic compounds to ions of metals. Since the reaction of metal ions with certain functional groups of organic compounds is reversible, immobilized metal ions can be used as a sorbent.

Recently the collapsed monomolecular films, obtained by Langmuir-Blodgett method, were proposed as sorbents for IMAC. This method allows to obtain structures with predetermined properties. Thus, the films represent a structure with the surface, composed with metal ions, bound to a solid. So such structures are capable of entering into a variety of interactions that allows us to use them as new metal affinity sorbents.

Monitoring and control of organic pollutants coming from the health sector in the environment are becoming topics of growing concern in recent years as they have been detected in all environmental compartments worldwide. Pharmaceutical residues can reach soils *via* animal excretions, sewage sludge spreading, manure application or wastewater irrigation to agricultural land, and they can reach the groundwater by infiltration. The occurrence of these emerging contaminants causes great public concerns because they could promote the proliferation of antibiotic-resistant strains of bacteria, disrupt the biotic environment and endanger human health.

Ciprofloxacin is widely utilized and difficult to be degraded in natural environment. So it was chosen as the most typical representative of fluoroquinolone group antibiotic.

Classical protocol of IMAC analysis includes sorption at $pH=3$. It was shown that there is no sorption of ciprofloxacin in the presence of acid, therefore we analyzed it in the presence of alkaline buffer and water. Under $0,1M$ ammonium bicarbonate buffer conditions the sorption was more than 30% , and in water - about 60% depending on the load on the sorbent.

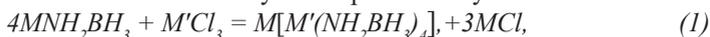
Synthesis of Complex Amidoboranes $M[M'(NH_2BH_3)_4]$ ($M = \text{alkali metal}, M' = \text{Ga, Al}$) by Metathesis

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Hydrogen energetics is suggested to be one of the most ecological. Investigation of acceptable hydrogen storage material that would fulfill all requirements is the challenging problem in this field. Metal derivatives of ammonia borane (NH_3BH_3 , AB) – amidoboranes (MABs) have been studied for last 15 years as potential hydrogen storage materials [1]. Although AB has higher hydrogen capacity relative to MABs, dehydrogenation temperatures of latter ones are quite lower and there is no release of borazine ($B_3H_6N_3$) as a volatile by-product and a very small amount of NH_3 . A new field of investigation includes complex amidoboranes: it was reported that decomposition of bimetallic ones might proceed without any undesired by-products [2, 3].

Thus there is also an interest how the metal influences on properties of complex amidoboranes. In this aspect, the pathway of synthesis complex amidoboranes by metathesis (1) was studied theoretically and experimentally:



where $M = Li, Na, K$; $M' = Al, Ga$.

DFT computations in the gas phase revealed that the metathesis is exergonic. For example, the calculated value of standard Gibbs free energy for reaction (1) in case of $M = Na$ and $M' = Al$ is -188 kJ/mol.

Reactions (1), where $M = Li, Na, K, Rb, Cs$ and $M' = Al, Ga$ were carried out in THF solution under the argon atmosphere in the glovebox IL-2GB or using the Schlenk line. Products were characterized by solid state and solution NMR spectroscopy.

Acknowledgements. Financial support from Russian Science Foundation grant 14-13-00151 and equipment of the resource “Centre for Magnetic Resonance” of SPSU are gratefully acknowledged.

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Determination of Synthetic Water-Soluble Colorants in Cough-Cold Formulations by Sequential Injection Chromatography

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Synthetic colorants are included in various dosage forms of pharmaceuticals for the purpose of producing an eye-appealing product. Their structures consist of azo groups and benzene or naphthalene rings, thus they can induce allergic reaction, cancer diseases or attention deficit hyperactivity disorder – like behavior in children. The control of synthetic colorants in pharmaceuticals is of great importance.

Nowadays analytical chemistry is focused on the miniaturization and automation of analytical procedures. Sequential injection chromatography (SIC) fits for the purpose with simple and portable manifold, user friendly operation, and reduced mobile phase consumption and waste production.

This work is devoted to the development of rapid chromatographic separation and determination of synthetic water-soluble colorants (Sunset Yellow FCF, Carmoisine and Green S) in cough-cold formulations. Two monolithic columns (Chromolith® CN 50-4.6 and Chromolith® Diol 50-4.6, Merck) were tested. Mobile phase composition (water, ammonium acetate and acetonitrile), volume, gradient profile and flow rate were optimized for each column. Spectrophotometric detection was set to 480, 516 and 630 nm, respectively. Analytical characteristics of developed method and benefits of selected columns for SIC will be discussed.

Acknowledgements. Authors gratefully acknowledge The Russian Foundation for Basic Research, The Russian Government, The Russian Scientific Foundation, The Czech Science Foundation and International Visegrad Fund (projects no. 15-33-20068, MD-6597.2016.3, 16-33-50090, P206/15/10781S and 16-13-10117) for partial financial support of this work.

Design of an Optical Sensing Platform for Determination of Physiological Cations in Microliter-Size Biological Samples

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Optochemical sensors (optodes) are promising instruments for the analysis of biological objects, and are successfully utilized for investigation of tissues, living organisms, and even single cells. In contrast to the commonly used analytical methods, optodes allow of performing nondestructive analysis, they do not require power supply and physical connection with the detector. All this opens great possibilities for the miniaturization of the optode-based devices as well as of the measurable samples.

This work is aimed at the development of a platform of optical sensors for simultaneous determination of the most important body cations (Na^+ , K^+ , Ca^{2+}) in small volumes of biological liquids.

New colorimetric sensors have been developed based on the plasticized PVC membranes containing ionophores and lipophilic pH indicator (chromoionophore). Quantitative composition of the membranes was optimized for the physiological range of analyte concentrations. A novel approach for the composition optimization was developed based on mathematical analysis of the implicit sigmoid response function of an optode and its respective derivatives. The influence of the active components concentrations and their ratios on the optical response was carefully studied. The approach allowed to optimize *a priori*

the response range and span of the optodes for determining Na^+ , K^+ , Ca^{2+} for the desired concentration range, namely for the physiological levels in human saliva. Dynamic range, response time and hysteresis of the optical response were evaluated. Optodes were assembled in a platform (inset in Fig. 1), which demonstrated the optical response in physiological range of concentrations in mixed solutions (Fig. 1). Simultaneous determination of sodium, calcium, and potassium cations was successfully performed in spiked water samples and real samples of saliva.

The developed platform can be implemented for the express analysis of biological samples in the intensive care units and ambulance cars without involving the hospital central laboratory.

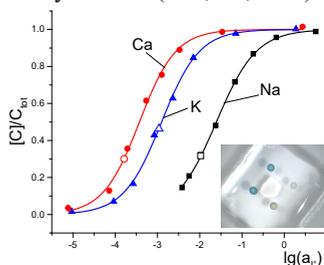


Fig. 1. The response of the optochemical platform in the multicomponent solutions (solid symbols); the results of determination in diluted saliva (empty symbols).

Modeling of Co-Distribution of Sodium Asparaginate and Isoleucine in Aqueous Solution of Ionic Liquid Surfactant

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Micellar liquid chromatography (MLC) is one of the perspective methods of separation bioorganic compounds. Particularly, micellar chromatography is great way to separate amino acids, carbohydrates, vitamins etc.[1, 2] Coefficient of distribution between micellar pseudo phase and intermicellar aqueous solution is very important parameter of MLC. Prediction of this coefficient in computer simulation allows to choose optimal parameters for separation: solvent, surfactant, and concentration.

In this research we considered systems, which contain micelle of 3-dodecyl-1-methyl-imidazolium bromide ($[C_{12}\text{mim}]\text{Br}$) in presence of aqueous solution of sodium asparaginate and isoleucine. Molecular dynamics simulation were carried out by GROMACS software package. Concentration of $[C_{12}\text{mim}]\text{Br}$ was 0.2M (CMC is 0.1M), concentrations of amino acids were varied (0-0,09M).

We used parameters of force field CHARM27-AA (Chemistry at HARvard Macromolecular Mechanics), to describe surfactant molecules and force field OPLS-AA AA (Optimized Potential for Liquid Simulations) to describe amino acids [3].

As a result the coefficients were obtained for each system. Amino acids concentrated in the different regions of micelle(micellar crown, palisade) depend on their hydrophobicity.

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Automatic Static Tensimeter for Studying Equilibrium and non-Equilibrium Processes

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We introduce an automatic tensimetry apparatus to study chemical processes in a closed glass system in equilibrium or not equilibrium conditions, such as vaporization, thermal decomposition or complex dissociation.

As our tensimeter derives from the static tensimetry method with a glass membrane null-manometer [1], it allows carrying out measurements in a temperature interval range of $-200 \div 1000$ °C and pressure range of $0 \div 800$ torr. Pressure changes in a reaction chamber causes displacement of a thin glass membrane, so the pressure value inside the chamber can be calculated. We use a new approach to determine a position of the membrane, that includes using Hall effect sensor (Fig. 1). The sensible sensor alongside with automated rapid data acquisition allows lower systematic and random errors.

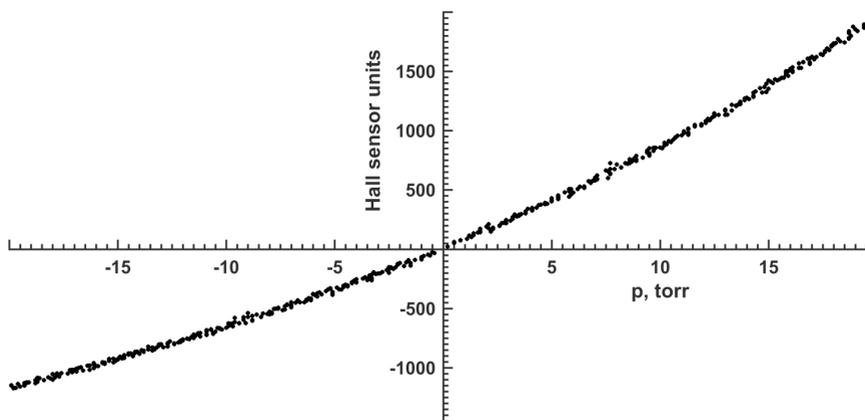


Fig. 1. Dependence of sensor readings on the pressure difference.

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Arc Atomic Emission Spectral Analysis of Potato without Sample Mineralization

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Potato is one of the most consumed foodstuffs in the world. For example, in Russia various agricultural companies in 2015 collected 7.3 million tons of potatoes. There are also many food products, prepared from potato. Potato is rich of many essential macro- and microelements, which passed from soil during growth. However, in case of farming on contaminated area or using some fertilizers and pesticides, potato accumulate heavy metals that can cause serious harm to human body. For instance, lead disrupts the functioning of brain and central nervous system, causing coma, convulsions and even death. Cadmium has a toxic effect on the kidneys, bones and respiratory system. That is why for each substance harmful to the body there is the maximum allowable concentration. In this regard, it is important to determine macro- and microelements content of potato for evaluation of its nutritive value and toxicological safety.

For food products, including potato, there is a variety of techniques developed for the determination of microelements. Unfortunately, the majority of them requires sample mineralization before the analysis, which has some drawbacks such as long duration, high risk of the sample contamination and increase of error of analysis results. Moreover, most of procedures are pointed at the determination of small set of elements. The aim of this work is the development of the arc atomic emission technique of determination of macro- and microelements in potato without sample mineralization.

This report presents the results of studying the influence of sample weight, electrode shape, interelectrode distance, and current strength of arc discharge on intensity of spectral lines and signal-to-noise ratio for improvement of metrological characteristics. This investigation was made using model samples as well as real potato samples. Results of qualitative analysis of potato are also presented.

Bioactive Magnetic Composite Nanomaterials

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Magnetic composite nanomaterials with enzymes attracting a lot of attention as a drug delivery systems for therapeutic needs or as an immobilised catalyst in industry. Typical composition of such system consists of enzymes entrapped in silica cage with co-entrapment of magnetite nanoparticles for magnetic properties. Despite the fact that this field is developing fast, real application of such materials in medicine faces one major problem: silica still doesn't have an approval for parenteral administration.

Here we present a new class of two-component magnetic biocomposites obtained through entrapment of enzymes into pure magnetite matrix. For this purpose a pure stable hydrosol of non-coated magnetite nanoparticles at neutral pH was developed. A set of therapeutic enzymes (carbonic anhydrase (CAB), horseradish peroxidase (HPR) and acid phosphatase (AcP) was entrapped into resulting xerogel matrix. Entrapped enzymes showed higher thermal stability and bioactivity compared to free enzymes in solution at elevated temperatures. For instance, denaturation temperature of entrapped CAB was 30 °C higher than for free enzyme, for AcP and HRP denaturation temperatures was 25 and 22 °C higher respectively. The whole composition of obtained materials is fully biocompatible and approved for parenteral administration. High magnetic moments of such composite materials and remarkable stability make these nanocomposites promising as potential therapeutic agents or for needs of industry. The work is supported by grant MK-9109.2016.3.

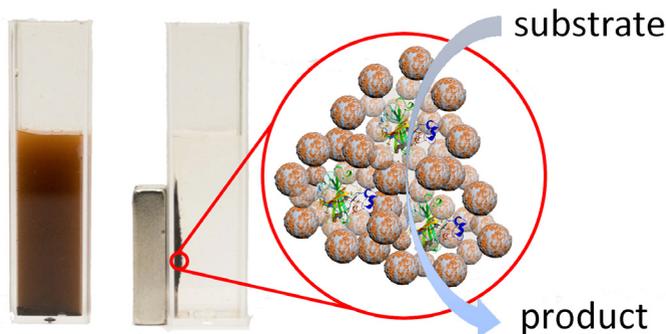


Fig.1. Nanocomposite could be manipulated by magnetic field.

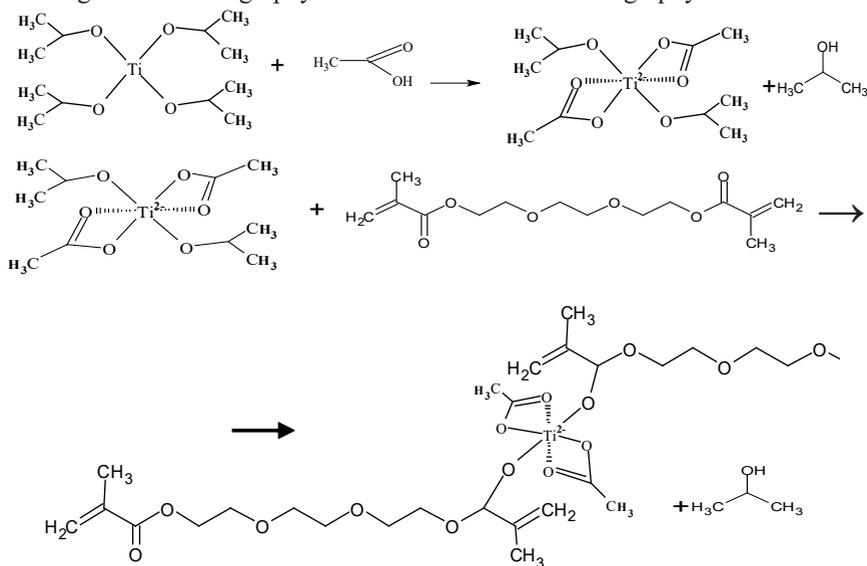
Synthesis of High Refractive UV-Hardening Polymers

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The invention of new materials is fundamental problem of each field of science and technology. Creating such objects as optical waveguides, capsules for light-emitting diodes and special optics coatings needs materials with specified properties. Refractive materials prepared on the base of oligoether acrylates and chelating complexes of titanium have refractive index in curved state 1.85. The isopropanol was used for controlling rheological properties of substance.

HRI composite material are prepared such a way that is stable up to 3 months at room temperature storage conditions and can be easily processed by Meyer bar coating and subsequently UV-cured. New composite was successfully tested by making rainbow holography with method of smooth lithography.



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Synthesis and Photophysical Properties of Iridium(III) Isocyanide Complexes

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Among platinum group metals, palladium and platinum isocyanide complexes are well recognized [1]. In this context, iridium-isocyanides attracted much less attention [2].

In the course of our studies on chemistry of metal-isocyanide derivatives, we have synthesized several new iridium(III) isocyanide complexes $[(ppy)_2IrCl(CNR)]$ (**4**, **5**) and $[(ppy)_2Ir(CNR)_2](CF_3SO_3)$ (**6**, **7**) ($ppy = 2\text{-phenylpyridine-}C^2,N'$). Indeed, the complexes **4** and **5**, were prepared starting from the binuclear complex $[(ppy)_2Ir(\mu\text{-Cl})_2]_2$ upon reaction with one equiv of appropriate CNR in refluxing CH_2Cl_2 (yields 82–87%). The corresponding *bis*(isocyanide) species **6** and **7** were generated from $[(ppy)_2IrCl(CNR)]$ upon chloride abstraction with CF_3SO_3Ag in a CH_2Cl_2 and followed by addition of equiv of CNR (R = Xyl, Mes) in CH_2Cl_2 (yields 76–79%). The photophysical properties of this compounds were studied in CH_2Cl_2 solution.

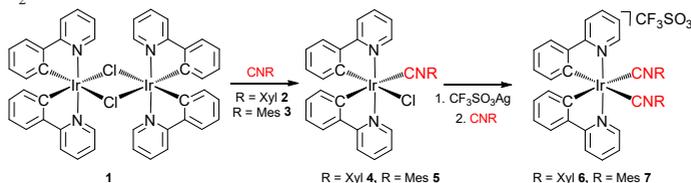


Fig. 1. Scheme of synthesis iridium isocyanide complexes.

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

Acknowledgements. The authors thank RFBR (16-33-60123) and Grant of Russian Federation President (MK-7425.2016.3). The authors are grateful to the Center for Magnetic Resonance, Center for X-ray Diffraction Studies, Center for Chemical Analysis and Materials Research and Center for Optical and Laser Materials Research and Chemistry Educational Centre (all belong to Saint Petersburg State University).

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Interatomic Interactions and the State of the Iron Atoms in Lanthanum Gallate Doped with Strontium and Magnesium

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Nowadays doped lanthanum gallate is one of the most perspective materials for creation of solid oxide fuel cells (SOFC). Perovskite-like structure of LaGaO_3 allows the synthesis of solid solutions over a wide range of concentrations. Depending on the nature and the quantities of dopants lanthanum gallate can be used as ionic and/or electron-ionic conductor with a high value of conductivity.

The goal of this research is to study the influence of the quantity of dopants (Sr, Mg) on the state of iron atoms and intermolecular interactions. The magnetic, conductive and structural characteristics of lanthanum gallate doped with iron, magnesium, and strontium were explored over a wide range of concentrations.

The samples of the research were two solid solutions: $\text{LaFe}_x\text{Ga}_{1-x}\text{O}_3$ and $\text{La}_{1-0.2x}\text{Sr}_{0.2x}\text{Fe}_x\text{Mg}_{0.2x}\text{Ga}_{1-1.2x}\text{O}_{3-\delta}$ ($x = 0.01 - 0.1$). They were synthesized by ceramic procedure and appeared to be single-phase according to the X-ray diffraction method (S.G. *Pbnm*). The obtained dependence of the unit cell parameters on the concentration of dopants correlated with the Vegard law.

Magnetic susceptibility was measured in the temperature range from 77 to 400 K, and the values of paramagnetic component of magnetic susceptibility and of the effective magnetic moment depending on the concentration of iron in the solid solution were defined. Anomalous values of the effective magnetic moment in the infinitely diluted solid solutions point to the formation of high nuclearity clusters containing iron atoms and also magnesium, strontium and associated vacancies. Specific magnetization was measured in the temperature range from 2 to 400 K in FC and ZFC modes. Magnetic hysteresis was measured in the range of magnetic fields from -50 to +50 kOe for the temperatures 5, 100 and 300 K.

Mossbauer spectroscopy investigation was used to explore the state of iron atoms. The experiment was carried out on specially synthesized samples, enriched with ^{57}Fe . The obtained spectra were described by one singlet and one doublet. A singlet could be assigned to single iron(III) atoms in the symmetric surrounding. A doublet could be assigned to high-nuclearity clusters of iron atoms. The dependence of conductivity on temperature is typical for semiconductors and for similar systems of solid solutions. It was found that for the system with strontium and magnesium the values of conductivity are higher than for the iron only system.

Acknowledgements. The studies were performed at the Research Park of St. Petersburg State University.

Effect of Ionic Association in the Response of Ion-Selective Polymeric Optochemical Sensors

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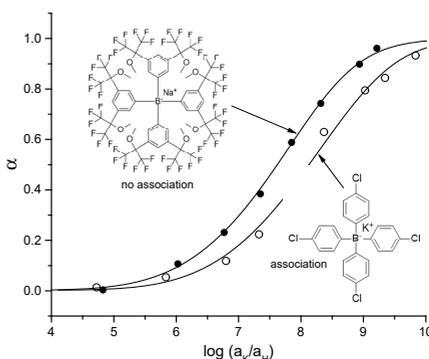
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Ion-selective polymeric optical sensors (optodes) transmit activity of an ionic analyte into the optical signal. As chemical sensors optodes provide non-destructive analysis and at the same time can be miniaturized down to nanometer-size that is why they became perspective instrument of quantitative microanalysis. The sensors are composed of ionophores, lipophilic pH indicator dyes and ionic additives incorporated into a plasticized polymeric membrane. Ionophores extract the analyte from the sample into a polymeric bulk of the membrane. Meanwhile the indicator changes its protonation degree.

Despite that the anionic additives are always present in the membrane phase providing its ion-exchange capacity, the ion-pair formation between the cationic analyte and the anionic species is neglected in the well recognized concept of the optode response [1].

Here we demonstrate, for the first time, how the association in the polymeric optode phase influences the optical response. We show theoretically and experimentally that the association significantly alters the working range and the sensitivity of the optode response of a pH/pK optodes based on the same chromoionophore ETH 2439 but with different ionic additives (see the Fig.). The consideration of the association effects allowed for a quantitative estimation of association constants *in situ* in the polymeric phase.

We show that the explicit response equations can be derived for the pH-sensing optode membranes where the metal ion or the protonated indicator form ion pairs with the cation exchanger. Limiting cases of fully dissociated and strongly associated membranes are discussed. The optode response is simulated with no assumptions on the association degree of any type of the species present in the membrane phase.



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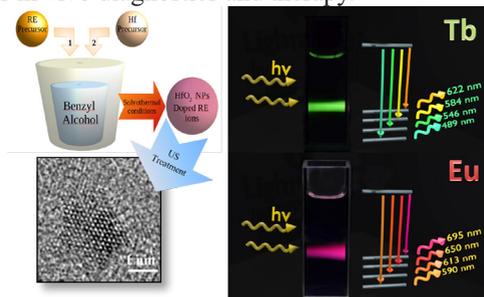
Hafnia Based Injectable Luminescent Nanocolloids

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Quantum dots (QD) are well known as the major tool in bioimaging and different bioapplications, but are still highly toxic. There are several ways to reduce QD toxicity, for example, by creation of biocompatible coatings, but anyway QDs could not be approved for medical applications due to presence of a toxic core. Luminescent nanoparticles (NPs) based on hafnia could be a good alternative to QDs in this area. Hafnia NPs is considered as fully biocompatible material and have FDA approval for cancer radiotherapy.¹ However, pure hafnia colloids can not be used for this purpose due to isoelectric point closed to pH level of human blood thus leading to problems related to fast coagulation.

In this work, we describe a potential solution of this problem by introducing luminescence activators ions into the crystal lattice of bioinert and transparent hafnia nanocrystals. The doped hafnia NPs were obtained via one-step sol-gel method. According to TEM, SEM and XRD data, doped NPs have high-temperature cubic form with uniform particle size distribution of 2-3 nm. The NPs doped with Tb(III) ions have a number of characteristic emission peaks at 490, 548, 584 and 622 nm. The Eu(III) doped NPs emit energy in the red region: 590, 613, 650 and 700 nm. The samples are stable in water, Ringer's solution and human plasma. It was shown, that obtained luminescent nanocolloids doesn't effect on a coagulation process of normalized human plasma, thus potentially could be directly injected in a human body. Overall, the doped NPs are inert in biological system models, and at the same time they have strong luminescence characteristics, which make them promising for in vivo diagnostics and therapy.



Synthesis procedure of hafnia and luminescent properties.

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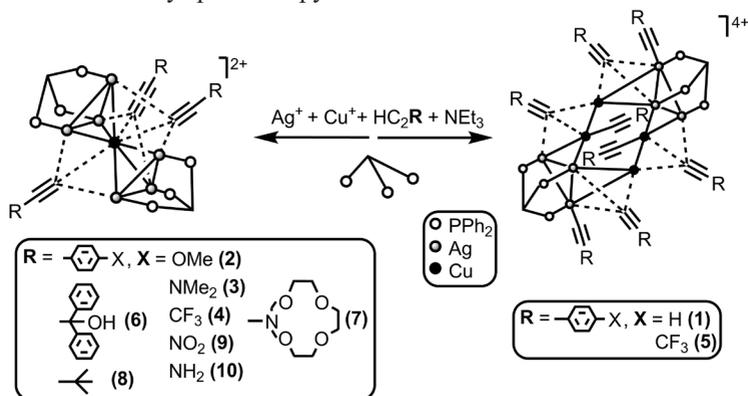
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Synthesis of Novel Alkynyl-Phosphine Cluster Complexes with $\{Ag_xCu_x\}$ Metal Core ($x = 1, 4$)

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Phosphorescent alkynyl-phosphine heterometallic cluster complexes with metal core $\{Ag_xCu_x\}$ are using successfully in organic light-emitting diodes (OLEDs) field because of highly efficient electroluminescence [1]. Moreover, homometallic analogues based on 1,1,1-tris(diphenylphosphino)methane (tppm) have been obtained in our research group earlier [2]. We report herein synthesis of extended series of alkynyl-phosphine complexes with $\{Ag_xCu_x\}$ metal core ($x = 1, 4$) based on tppm. Reaction between $AgSO_3CF_3$, $Cu(NCMe)_4SO_3CF_3$, tppm, and acetylenes in the various molar ratio in acetone in presence NEt_3 under nitrogen atmosphere at r. t. resulted in the compounds **1-10** formation in good (85-96%) yields. All clusters obtained showed the various structural motifs of the metal core and were fully characterized by spectroscopy methods.



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

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Experimental Investigation of Chemical Equilibrium in the System with Reaction of Ethyl acetate Synthesis under Polythermal Conditions

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Ethyl acetate industrial production is based on acid-catalyzed esterification of acetic acid with ethanol which is combined with the stage of separation. Such coupled process requires accurate data on thermodynamic properties of the system acetic acid – ethanol – ethyl acetate – water, especially data on chemical equilibrium (CE) and the values of thermodynamic constant of CE (K_a).

In this work we present experimental data on CE in the system with ethyl acetate synthesis reaction at 313.15 K, 323.15 K and atmospheric pressure in wide composition range. Two analytical methods were used for investigation of CE: gas chromatography (GC) and nuclear magnetic resonance (NMR). Experimental methods were compared and it was found that GC data are in a good agreement with NMR data. The sets of new experimental data gave the opportunity to present in more detail the surfaces of CE in composition tetrahedron (Fig. 1) and reliable values of thermodynamic constant of CE. The values of thermodynamic constant of chemical equilibrium at 313.15 K and 323.15 K were determined using NRTL model and experimental data:

$$K_a = 4.6 \pm 0.4 \text{ at } 313.15 \text{ K and } K_a = 4.2 \pm 0.3 \text{ at } 323.15 \text{ K.}$$

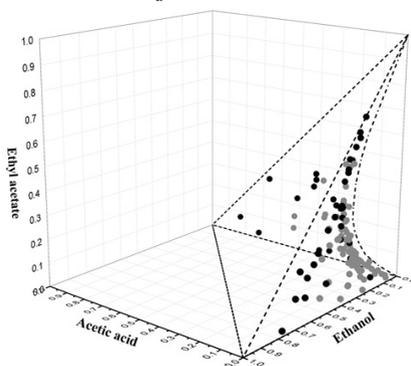


Fig. 1. The surface of chemical equilibrium in the system acetic acid – ethanol – ethyl acetate – water at 323.15 K: ● – compositions determined by GC analysis, ● – compositions determined by NMR method.

Acknowledgements. The reported study was funded by RFBR according to the research project No. 16-33-00129 МОЛ_a.

Platinum(II)-Mediated Addition of Thiazol-2-Amines to Isocyanides

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Coordination of isocyanides to metalcenters leads to dramatic change in their reactivity. As a result, possible becomes the addition of weak NH-nucleophiles to triple bond CN, which normally does not proceed under mild conditions. This allows to synthesize acyclic diaminocarbene complexes of transition metals, that are difficult to obtain by other methods.

Previously in our research group, it was found that coupling of Pd(II)-isocyanide complexes with thiazol-2-amines leads to formation of carbene complexes, which can act as nucleophiles themselves and capable of attacking one more isocyanide complex, forming binuclear species.

In this work we studied the interaction between Pt(II)-isocyanide complexes with various thiazol-2-amines. We have found that depending on reaction conditions and the structure of the initial reagents, different products may be obtained: classic monocarbene complexes (cationic **1**, neutral **2**), *bis*-carbene complexes **3**, or binuclear complexes **4,5** (Fig. 1).

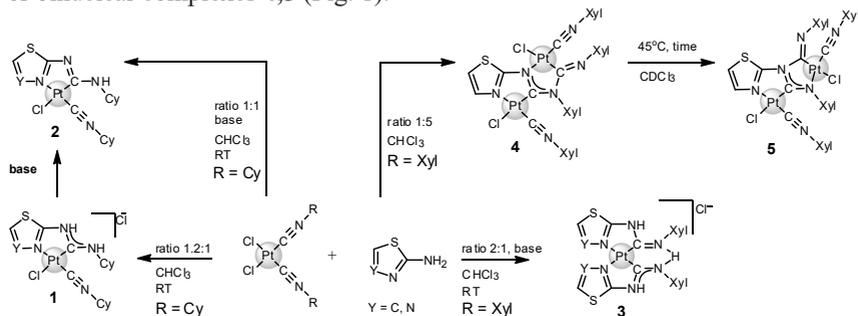


Fig. 1. Coupling of Pt(II)-isocyanide complexes with thiazol-2-amines under different conditions.

Acknowledgements. This work was supported by SPbU (grant 12.37.214.2016). Physicochemical studies 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 SPbU).

Complexes of AlBr_3 with Bifunctional N-donors: New Structural Type for 1:1 Composition

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Complexes of group 13 metal halides with polydentate nitrogen containing donors are prospective single-source precursors (SSP) for the synthesis of nitrides by the chemical vapor deposition method [1]. Stability and volatility are the key characteristics of a successful SSP. Since structure of potential precursors determines the volatility of the complexes, its identification is an important task [2].

In the present report we experimentally established crystal structures of two new complexes of AlBr_3 with 1,2-bis(4-pyridyl)ethylene (bpe). The molecular structure of $2\text{AlBr}_3 \cdot \text{bpe}$ complex where bpe serves as bridging ligand is analogous to the complexes of group 13 halides with pyrazine [3] and 4,4'-bipyridine [4]. In case of initial 1:1 stoichiometric ratio the ionic $[\text{Al}_3\text{Br}_8(\text{bpe})_3][\text{AlBr}_4]$ complex has been formed. In $[\text{Al}_3\text{Br}_8(\text{bpe})_3]^+$ cation Al atoms adopt both octahedral and tetrahedral environments. This complex belongs to new structural type of group 13 metal halides complexes with bifunctional N-donors.

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

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Engineering Nanoporous Iron(III) Oxide Into an Effective Water Oxidation Electrode

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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. Here, we demonstrate that iron oxide, the most abundant and least expensive transition metal compound, can be used as a catalytically active surface for the four-electron water oxidation to O_2 at neutral pH which represents the kinetic bottleneck of the overall reaction.¹⁻² Nanotubular iron(III) oxide electrodes are optimized for catalytic proficiency in the water oxidation reaction. Nanostructured electrodes are prepared from anodic alumina templates coated with Fe_2O_3 by atomic layer deposition. Scanning helium ion microscopy, X-ray diffraction and Raman spectroscopy characterize the morphology and phase of samples submitted to various treatments. These methods document the contrasting effects of thermal annealing, on the one hand, and of electrochemical treatment, on the other hand. The electrochemical performance of the corresponding electrodes is quantified by steady-state electrolyses and electrochemical impedance spectroscopy. A rough and amorphous Fe_2O_3 with phosphate incorporation proves to be optimal in the water oxidation reaction. The combination of electrochemical treatments with the “anodic” pore geometry delivered an effective turnover increase by a factor of 540 with respect to a smooth, planar Fe_2O_3 surface.

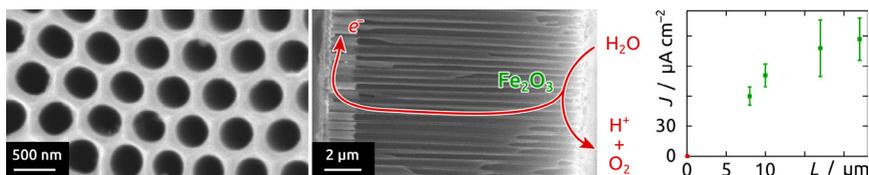


Fig. 1. Nanostructured Fe_2O_3 electrode in top view (left), in cross section (middle) and the corresponding water oxidation performance at pH 7 at 0.49 V applied overpotential η .

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“Antenna Effect” of {Au} Acetylene Complexes towards Ln^{III} Ions

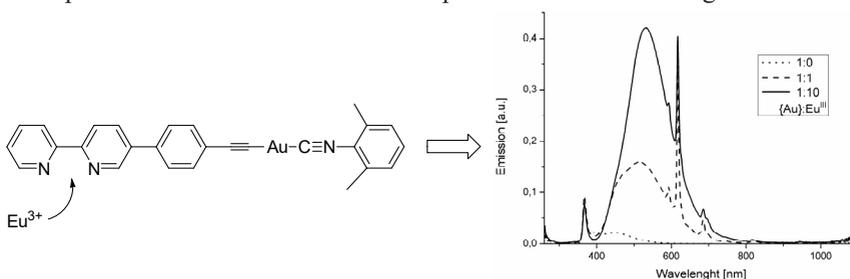
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For a {Au} acetylene complex [RC≡CAuL] (R: 5-phenyl-2,2'-bipyridine; L: 2-isocyano-1,3-dimethylbenzene) the “antenna effect” for Eu^{III} could be observed. Absorption and emission spectra of the {Au} complex were measured in a DCE solution and it was titrated with a MeCN solution of [Eu(NO₃)₃·6H₂O]. In the emission spectra sharp bands which are characteristic for Eu^{III} are visible at a ratio of {Au}:Eu^{III} ≈ 2:1. With increasing concentration of europium this bands reach higher intensities and the maximum of the emission band of the complex is shifted to longer wavelength (red shift). In contrast to this a solution of pure [Eu(NO₃)₃·6H₂O] shows no emission in the measured parameter area (concentration and wavelengths). In the absorption spectra a red shift of the absorption maximum of the complex occurs with increasing amount of Eu^{III}.

Comparison the emission spectra of degassed and aerated solutions showed that the intensity of the europium signals is higher for the degassed solutions. Excitation spectra were taken at 530 and 614 nm where the latter shows a sharp band at 306 nm which is characteristic for europium. Both measurements were performed with ten times excess of Eu^{III} compared to the amount of the {Au} complex.

Absorption spectra for titrations of the {Au} complex with solutions of [Ln(NO₃)₃·nH₂O] of NIR emitting lanthanides (Ln = Nd, Er, Yb) showed already a red shift of the absorption maximum comparable to the one of europium. Therefore, we hope that this “antenna effect” is also possible for NIR emitting lanthanides.



Acknowledgements. The authors (H.H.) appreciate financial support from PROMOS scholarship program (DAAD). All measurements were performed using the following core facilities at St. Petersburg State University Research Park: Centre for Magnetic Resonance and Centre for Optical and Laser Materials Research.

A Gas Chromatographic-Mass Spectrometric Analysis of the Metabolite Composition of *Potamogeton perfoliatus* L

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A gas chromatographic-mass spectrometric analysis of the essential oils of perfoliate pondweed (*Potamogeton perfoliatus* L.) from different lake habitats, which differ by the level of anthropogenic load was undertaken for the first time to identify qualitative and quantitative composition of low molecular weight volatile organic compounds (VOCs). The samples of *P. perfoliatus* were collected from 5 lakes of the Karelian isthmus. Essential oils containing VOCs were obtained from the dried plants by steam hydrodistillation for 6 hours using a glass Clevenger apparatus. Chemical composition of essential oils was examined by GC-MC. Essential oil of *P. perfoliatus* from different habitats contains from 54 to 115 VOCs, indicating a high variability of the component composition of metabolites depending on growing conditions of plants. The highest number of VOCs was recorded in macrophytes located in undisturbed habitats. *P. perfoliatus* from habitats with the highest anthropogenic load had the lowest total content of the VOCs. 30 components were basically the same in 5 plants' essential oils. 2-Hexenal, dibutyl phthalate, hexadecenoic acid, phytol, 9,12,15-octadecatrienoic acid were the major components. The greatest differences in the composition of the VOCs of *P. perfoliatus* was observed between undisturbed aquatic habitats and habitats with significant anthropogenic pressure.

Solution Properties of Hyperbranched Poly(Methyl Methacrylates)

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Molecular properties of hyperbranched macromolecules-nanoparticles [1] obtained by copolymerization of methyl methacrylate (MMA) with the branching agents *m*-ethyleneglycol dimethacrylates (EDMA) at $m = 1$ and $m = 3$, have been studied in diluted solutions. Dynamic light scattering, viscometry, and dielectric spectroscopy have been used for the study. By means of comparison with the linear poly(methyl methacrylates) it is shown that conformational properties of these macromolecules can be characterized as the intermediate between statistical Gaussian coils of linear polymers and dendrimers. Their hydrodynamic behavior in solution does not correspond to solid unpenetrative nanoparticles. The influence of the length of branching agent on kinetic properties of hyperbranched copolymers of methyl methacrylate with *m*-ethyleneglycol dimethacrylates has been established.

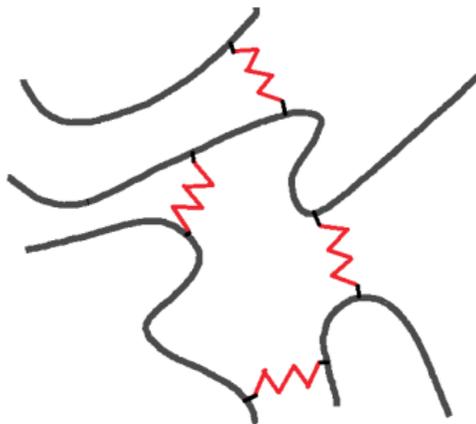


Fig. 1. The model of hyperbranched copolymer MMA-EDMA. Solid lines correspond to poly(methyl methacrylate) fragments and zigzag bridges correspond to the chains $-O-CH_2-CH_2-O-$.

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Molecular Simulation Study of Structure-Diffusivity Relationships in Yttria-Stabilized Zirconia

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Yttria-stabilized zirconia (YSZ), $[\text{ZrO}_2]_{1-x}[\text{Y}_2\text{O}_3]_x$, is a popular electrolyte for solid-oxide fuel cells due to its high ionic conductivity. This ability arises due to the doping of ZrO_2 by other oxides, such as Y_2O_3 . Replacement of Zr^{4+} ions by Y^{3+} ions leads to the formation of vacancies in anionic sub-lattice due to the electroneutrality condition, thus enabling the hopping of O^{2-} ions to vacant sites in the lattice. Ionic conductivity of YSZ is strongly influenced by composition of the material and operating temperature. The effects of these factors can be studied in detail by atomistic computer simulations.

In this work we report the results of a detailed computer simulation study of the dependence of O^{2-} diffusion on the structure of YSZ samples. Diffusion of ions was studied for YSZ containing from 1 to 12 mol. % of Y_2O_3 for temperatures between 1200 K and 2000 K using the molecular dynamics method. Simulations were carried out in the NVT ensemble with a total run length of 2–4 ns. Simulated samples represented bulk cubic phase and were comprised of $5 \times 5 \times 5$ unit cells containing a total of 1446–1495 ions. The dependence of diffusivity on structural parameters was studied by considering at least 20 different random distributions of Zr^{4+} and Y^{3+} ions for each YSZ composition. This approach allows for sufficiently accurate averaging of diffusivity data, while preserving the possibility of performing detailed analysis of structure-property relationships. Structural features of simulated YSZ samples were described by radial distribution functions and cation-cation and cation-anion coordination numbers.

Simulation results demonstrate that the averaging of diffusivity data over multiple random configurations greatly reduces the large uncertainty (up to 25%) in the values of diffusion coefficients and provides for a significantly more reliable estimation of diffusion activation energies. It was found that oxygen diffusion coefficients tend to increase for systems with uniformly distributed yttrium ions, while their clusterization is believed to be cause of diffusion hindering. Diffusion activation energies were shown to increase monotonically over the whole range of compositions considered in this work. The dependencies of oxygen diffusion coefficients on temperature and YSZ composition are generally in line with the data reported in the literature.

Molecular Simulation of Gas Adsorption in CMK-5 in the Presence of Acetonitrile

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Adsorptive separation of gaseous mixtures has been steadily gaining popularity over the last two decades. The use of porous solids for separation and purification of gases is a particularly promising approach for important industrial mixtures such as biogas (CO_2/CH_4) and flue gas (CO_2/N_2).

The goal of this work is to study gas adsorption in the carbon mesoporous adsorbent CMK-5 in the presence of acetonitrile by means of computer simulation. The simulations were performed using grand canonical ensemble Monte Carlo method at 298 K and pressures up to 70 atm. The adsorption of pure gases and CO_2/N_2 (1:1), CO_2/N_2 (1:5) and CO_2/CH_4 (1:1) mixtures was considered in this study. The amount of acetonitrile in the pores was 0%, 6% and 20 mass %.

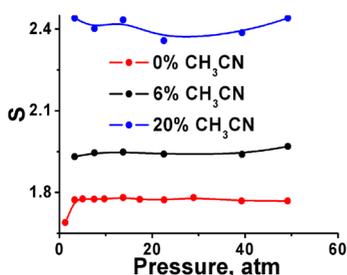


Fig. 1. The dependence of selectivity to CO_2 (S) on gas pressure.

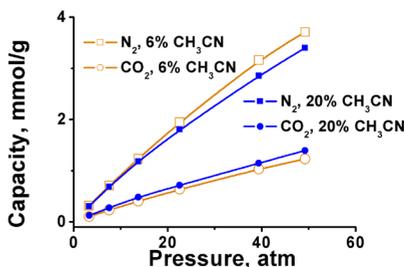


Fig. 2. Adsorption isotherms of gas mixture in the presence of different amounts of acetonitrile.

It was found that the selectivity of the adsorbent to carbon dioxide increases with increasing content of acetonitrile (Fig. 1). CMK-5 capacity for carbon dioxide in the presence of acetonitrile is also higher than in adsorbent without additives. Capacity for nitrogen, on the contrary, is lower in the adsorbent with acetonitrile (Fig. 2). Therefore acetonitrile can serve as a potential additive to the carbon adsorbent, which increases the efficiency of extraction of carbon dioxide from gas mixtures.

Kinetics of Fluorescein Release from Microgel-Liposome Complexes upon Temperature-Induced Collapse of Microgel

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Liposomes are spherical particles made of lipid bilayer with size ranging from tens to hundreds of nanometers. In addition to about a dozen of already approved liposome-based medicines, there are several hundreds of formulations being in different stages of clinical trials. Microgel (μG) is a micrometer- or submicrometer-sized particle composed of cross-linked polymer chains. Such particles can be made temperature and/or pH sensitive: they shrink (decrease in size) and swell (increase in size) in response to change in these parameters.

We propose to adsorb anionic liposomes ($D_{\text{eff}} \approx 60 \text{ nm}$) onto positively charged μGs ($D_{\text{eff}} \approx 350 \text{ nm}$) and then use temperature-induced collapse of μGs to trigger release of liposomal contents. Complexation was confirmed with Dynamic Light Scattering as aggregation occurs upon neutralization of μG surface charge upon adsorption of liposomes. At the same time, such μG -to-liposome ratio can be chosen so that aggregation is suppressed which makes the system applicable for drug delivery purposes. We further show that adsorption of liposomes onto μGs is not accompanied with release of liposomal contents (NaCl or fluorescein solution), in other words, liposomal membrane stays intact upon interaction with μG surface. Release of liposomal contents only takes place upon temperature-induced collapse of microgel.

Interestingly, it was found that kinetics of fluorescein release from liposomes depend on the structure of the collapsing μG -liposome complex. Fluorescein is released much faster when all the surface of μG particle is covered with liposomes (Fig. 1, left) in comparison to the complex where only a few liposomes are adsorbed onto each μG particle (Fig. 1, right). These findings are used to propose a mechanism for liposome contents release upon temperature-induced collapse of μG : the surface area of μG decreases dramatically, thus making the adsorbed liposomes to smash together. This leads to significant distortions of liposomal membranes (maybe even destruction of liposomes) and, as a result, significant increase in permeability.

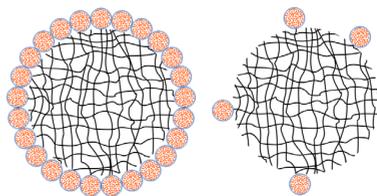


Fig. 1. Different structures of μG -liposome complexes.

Acknowledgements. This work was supported by Russian Science Foundation (project 14-13-00255).

Photoactivity and Catalytic Properties of Electrodes Modified by Metal Complexes with Schiff-Base Ligands

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The metal complexes with SalEn ligands are a relatively new class of organic complexes that is not fully studied [1]. SalEn ligands are tetradentate N_2O_2 Schiff bases with various substituents named so because of the simplest representative, N,N' -bis(salicylidene)ethylenediamine. Now it is known that $[M(\text{Shiff})]$ complexes possess a very useful property to modify a cathode submerged into their acetonitrile solutions under electrolysis with formation of poly- $[M(\text{Shiff})]$ film [2]. Properties of film obtained depend on nature of a central ion and a Schiff base ligand. Recently, a photoactivity of these films was found. And it should be clarified better by a number of methods such as cyclic voltammogram (CVA), using of different conditions of experiment.

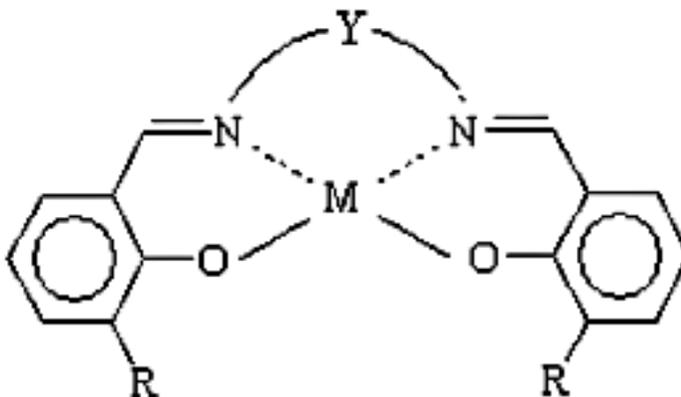


Fig. 1. General structural formula of $[M(\text{Shiff})]$ complexes.

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Synthesis and Characterization of Alginate Nanogels as a Drug Delivery System

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Nanogels based on natural biodegradable and biocompatible polymers for drug delivery are an area of active research. The aim of this work was to study a novel nanogels system formed from alginate and surfactants and to evaluate their potential for the association and delivery of drugs. The mean size of nanogels was influenced by nature of surfactant (anionic, cationic, nonionic) and by the alginate:crosslinker:surfactant mass ratio.

Morphology and structure characterization of nanogels was investigated by scanning electron micrographs (SEM). The results showed that surfactant nature influenced the formation of nanogels. It appears that nanogels with a diameter 80-110 nm was obtained by using sodium dodecyl sulfate (SDS) as surfactant.

In order to determine conditions suitable for the formation of nanogels we studied nanogels formation with different ALG/Ca²⁺/SDS w/w ratios. A high amount of Ca²⁺ ion gave the unstable nanogel the tendency to agglomerate due to increased electrostatic interaction between Ca²⁺ ion and surfactant. Meanwhile, the low amount of Ca²⁺ ion could not generate the formation of nanogel.

The further investigations showed that SDS concentration influenced the size of the resulting nanogels. In the case of high SDS concentration, due to agglomeration of nanogel, the observed nanogel possessing size less than 700 nm could not be obtained.

Bovine serum albumin (BSA) was chosen as a model drug. BSA was labeled with Cy3 and then incorporated into the nanogel with association efficiency of 33.6 % and loading efficiency of 1.5 %. BSA release from the nanogel was 29 % at pH 6.8 and 3 % at pH 5.0 for 24 h.

Acknowledgements. The research was supported by Russian Scientific Foundation (#14-50-00069_05-109).

Non-Enzymatic Electrochemical Sensors Based on Metal Microwires Produced by Laser-Induced Deposition

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The effective detection of glucose and hydrogen peroxide is a critical analytical goal due to its importance for many fields of science and industry, including clinical diagnostics, food processing, and pharmaceuticals. In particular, in clinical diagnosis and treatment of diabetes, which affects hundreds of millions of people around the world, determination of blood sugar level is vital [1]. Difficulties associated with production and use of enzymatic biosensors for detection of glucose and hydrogen peroxide encourage researchers to seek alternative solutions, including a huge number of papers in the last decade dedicated to the next generation of sensors - non-enzymatic ones. The fabrication of microelectrodes with a high specific surface area and electrocatalytic activity towards reduction of hydrogen peroxide and oxidation of glucose will allow to produce sensors for detection of these biologically substances.

The method of laser-induced metal deposition [2] was applied to synthesize nanostructured metal electrodes (Cu, Au, Ni, Au-Cu) for non-enzymatic glucose and hydrogen peroxide sensing. These electrodes were characterized by SEM, EDX, SIMS, XRD and EIS. Electrocatalytic activity of sensor platforms towards hydrogen peroxide and glucose was investigated by cyclic voltammetry and amperometry (Table 1).

Table 1. Sensory properties of electrodes.

	Cu-Au	Au	Cu	Ni
H ₂ O ₂ , LOD (µm/l)	0,025	0,025	0,5	-
H ₂ O ₂ , Linear response (µm/l)	0,025 - 10	0,025 - 1	0,5-60	-
Glucose LOD (µm/l)	0,025	0,025	0,1	20
Glucose, Linear response (µm/l)	0,025 - 5	0,025 - 50	0,1-100	20-40

Acknowledgements. The reported study was funded by RFBR according to the research project № 16-33-00645 and by the Saint Petersburg State University research grant (2015–2017, 12.38.219.2015).

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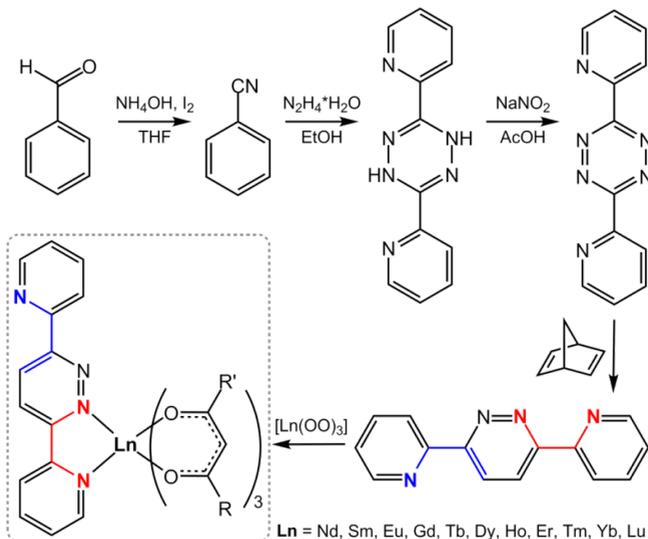
Synthesis and Luminescent Properties of Lanthanide Complexes on the Base of N⁴-Heterocyclic Politypic Ligand

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It is well known, that Ln^{III} emission is located in UV (Gd), visible (Tb, Sm, Dy, Eu) and NIR (Pr, Nd, Er, Ho, Tm, Yb, Lu) regions of spectra and it strictly depend on nature of the metal centre. At the same time key factor for developing of photoemission is sensitization of lanthanide luminescence by energytransfer from a strongly absorbing antenna group, which can be both organic compound and d-complexes. Thus a main point of creation of molecular emitters based on Ln^{III} ions is design of “antenna” with necessary stereoelectronic properties.

Herein we report the synthesis of Ln^{III} complexes with polytopic ligand containing heterocyclic fragments. Such polytopic ligand can be “antenna” and has a function for additional coordination of d-element, i.e. it is a candidate for design of d-f molecular assemblies.



Acknowledgements. The authors appreciate financial support from the Russian Science Foundation, grant 16-13-10064. All measurements were performed using the following core facilities at St. Petersburg State University Research Park: Centre for Magnetic Resonance, Centre for Optical and Laser Materials Research, Centre for Chemical Analysis and Materials Research, and X-ray Diffraction Centre.

A Complementary Theoretical and Experimental Approach to The Development of Metal-Organic Frameworks as a Novel Platform for Targeted Drug Delivery

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Conventional strategies to discovery of new drug delivery platforms requires a tedious experimental screening procedures. Modern computational chemistry techniques can tremendously facilitate such a search by providing an insight into the structure-property relationships for selected classes of materials and guiding thus the experimental studies. In this work we employed such a computations-aided rational design strategy for the development of a novel drug delivery platform based on bio-compatible. Among different materials available, metal-organic frameworks (MOF). Here, the interactions of the bio-compatible Fe-MIL-101 material with a heparin blood thinning drug were investigated in detail [1]. The directed synthesis creates systems with sensitivity to the pathogenic cellular environment and allows you to encapsulate the required drug and to ensure its controlled release. These tasks are accomplished in this study by a parallel and complementary theoretical and experimental programs aimed at a systematic investigation of selected MOF materials for their interaction and response to model drugs and bio-mimicking environments.

Density functional theory (DFT) calculations were carried out to establish correlations between the structural properties of MOF, their interaction with the encapsulated drug and their stability towards the components of physiological environment. Calculations were carried out at the PBE0/6-31+G(d,p) level of theory with implicit polarized continuum solvation model to account for the bulk effects in the aqueous system. Computations were carried out on cluster models of the Fe-MIL-101 material as a nanocontainer for heparin blood thinning agent. Calculations targeted the identification of the optimal parameters for the controlled decomposition of the hybrid MOF nanocontainer in biological fluids. We found that specific interactions between the heparin drug with the structural Fe centers of the MOF are key to the prolonged drug release and its enhanced pharmaceutical activity as is also evidenced by the parallel experimental studies. When the interaction between heparin and MOF are limited to weak dispersion-type bonds, no activity enhancement and controlled drug-release effect was observed.

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A New Generation of Polynuclear Homo- and Heterometallic Re-Based Species

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A great variety of luminescent Re(I) diimine tricarbonyls have been synthesized and intensively studied over the decades. These compounds have attracted a considerable attention due to their potential applicability in devices for luminescence sensing, OLEDs and in other fields such as catalysis. The eight novel polynuclear Re(I) complexes (shown in Fig. 1) were obtained and characterized in solution and the solid state.

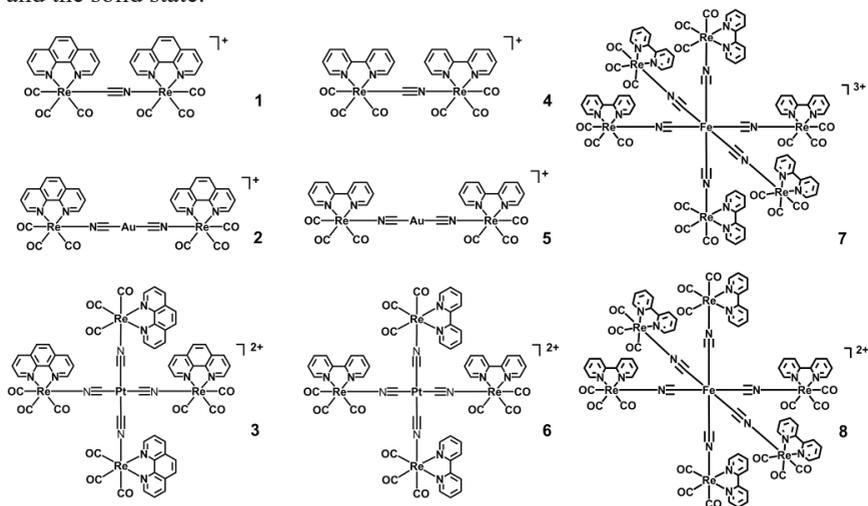


Fig. 1. Schematic representation of the Re(I) complexes 1–8.

It has been found that all compounds 1–6 are photoluminescent with moderate and high quantum yield in solution and in the solid state.

Acknowledgements. The author appreciate financial support from the Russian Science Foundation, grant 16-13-10064. The work was carried out using equipment of St.-Petersburg State University Research Park: Centers for Magnetic Resonance, Optical and Laser Materials Research, Chemical Analysis and Materials Research.

Radiocarbon Dating of the Bronze Age Sites of the North-Western Caucasus

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Caucasian dolmens represent a type of collective tomb architecture by being built using precisely dressed stone slabs and blocks. In terms of building construction they represent the varieties of chambered cairns. Dolmens in the Western Caucasus demonstrate an unexpectedly early example of regular ashlar masonry with a great variety of megalithic architecture [1]. The most common feature of the Caucasian dolmens is a relatively small (averaging c. 25-45 cm. in diameter) aperture (porthole) in the facade. The porthole ensured access to the burial chamber for periodic interments and always was closed by a stone plug. Yet the origins of dolmens remain unknown.

The important role for the chronological researches of the dolmens culture plays the radiocarbon method.

We collected radiocarbon dates produced by both conventional and AMS dating techniques were used in Saint Petersburg and Groningen Laboratories respectively. The dates were obtained from various materials. As a result, there is a good agreement between the stratigraphic information and the distribution of dates. Radiocarbon dates of the human remains covers the period (approx.) between cal. 1800 and 1300 BC with no signs of chronological gaps.

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Comparison of Different Sample Preparation Procedures for the Determination Microelements in Tobacco by Arc Emission Spectral Analysis

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Smoking is so deeply ingrained in our daily life that it is perceived as an ordinary event, not to attract attention. Most of the people know what damage to health nicotine and tar (basis of tobacco) make, as well as many other organic contaminants. Therefore, there is a fairly large amount of literature data about determination of the contents of these substances. But besides them tobacco contains heavy metals, which could provoke irreparable harm. As far as tobacco smoke is directly contacts with the lungs, these elements easily penetrate into the human organism.

Many heavy metals, such as Fe, Cu, Zn, Mo involve in biological processes and in certain amounts are necessary for the normal functioning of plants, animals and humans. On the other hand, excess of heavy metals may adversely affects living organisms. Moreover, some of heavy metals and their compounds are carcinogenic. Many metals can accumulate in tissues and organs, causing some diseases and disastrous impact on the human organism. Therefore, it is very important to be able to determine the content of heavy metals in order to monitor and control the product quality.

Almost all modern highly sensitive and most commonly used analytical methods require complex sample preparation, including mineralization of samples. In the literature there are a large number of substantially different (in duration, equipment and reactants used) performances of this step. The purposes of this study are the experimental comparison of different ways of sample mineralization, choosing the most preferred one with its subsequent optimization. Developed technique was verified by analysis of standard reference material of grass (due to the lack of tobacco standards). Results of identification of the tobacco elemental composition and assessment of the content of detected elements are also presented. Data in this study was obtained by means of alternative to ICP-AES and ET-AAS method – a.c. arc AES analysis of liquid samples, previously developed in our laboratory.

Acknowledgements .Part of the research was done using the equipment of the Educational Resource Center of Chemistry of Research Park of St. Petersburg State University.

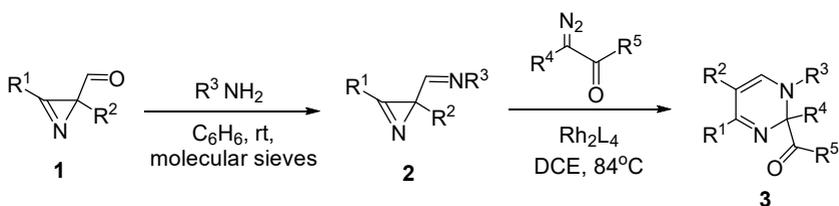
An Effective Two-Step Synthesis of 1,2-dihydropyrimidine-2-carboxylates from azirine-2-carbaldehydes and Diazo Carbonyl Compounds

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Functionalized dihydropyrimidine derivatives are well known as remarkable bioactive compounds for treating illness such as cancer, hypertension and other. Non-fused 1,2-dihydropyrimidines are considered to be less accessible compounds due to the limited number of synthetically useful reactions of both an 1,2-dihydropyrimidine ring formation and its functionalization.

In this work we suggest a new effective two-step procedure for the preparation of 1,2-dihydropyrimidine-2-carboxylates from easily available starting materials, 2*H*-azirine-2-carbaldehydes **1** and diazo carbonyl compounds **3**. This reaction sequence includes two steps: the transformation of aldehyde **1** into Schiff base **2** and of Rh(II)carbenoid-mediated 2*H*-azirine ring expansion. The most important features of the reactions of different diazo compounds are discussed. The reasons of unusually high regioselectivity of the second reaction step were clarified by use of quantum chemical calculations (DFT B3LYP/6-31+G(d,p)/ Stuttgart RSC 1997 ECP). From experimental and computational results also follows that synthesized 1,2-dihydropyrimidines exist in ring chain tautomeric equilibrium, represents a hidden form of 1,5-diazahexa-1,3,5-trienes.



$R^1 = Ar, Alk;$
 $R^2 = H, Me;$
 $R^3 = Ar, Alk, Ts;$
 $R^4 = Ar, COMe, CO_2Me, CN, CF_3;$
 $COR^5 = COMe, CO_2Alk.$

21 examples
up to 86% yields

Acknowledgements. The authors greatly appreciate financial support of RFBR (14-03-00187, 16-03-00596, 16-33-60130, 16-33-00651) and SPbSU (12.38.239.2014, 12.38.217.2015) grants.

Synthesis and Catalytic Properties of Individual and HAP-Supported Ni Nanoparticles

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Because of the unique magnetic, optical and electric properties, metal nanoparticles (NPs) have a wide range of application such as recording media, electronic devices, MRAM memories, nanosensors, medicine and other [1]. One of the most important fields of NPs application is catalysis. Ni NPs are perspective materials for the different types of industrial chemical reactions because they are cheaper than analogues and can be easily isolate by magnetic separation method [2]. But the approaches to control NPs size and shape - the parameters that directly affect the properties of nanoparticles – are still under discussion. Therefore, in this work the different stabilizers (organic acids and chelating agents) were used to inhibit the particle growth and the influence of its nature on NPs morphology, magnetic and catalytic properties were studied. Also Ni NPs were synthesized on the hydroxyapatite (HAP) NPs surface at different conditions to compare the functional characteristics of individual and supported NPs.

The Ni samples and HAP nanoneedles were obtained by polyol and precipitation method, correspondently, and characterized by XRD, SEM and SSA estimation. The magnetic properties were studied by VSM. The catalytic properties were investigated by UV-VIS spectroscopy using the model reaction of reduction of p-nitrophenol to p-aminophenol.

The obtained results show that the stabilizers form the chemical bond with the NPs surface, and improve the catalytic characteristics. For all the samples the induction period was observed wherein it values were lowest for the most chemically active stabilizers. This can be explained by the presence of the shell on NPs surface which didn't form the continuous coating. So NPs are prevented from oxidation and retained the ability to participate in catalysis reactions. The HAP supported NPs are demonstrated the similar catalytic behavior.

Scientific researches were performed at the Centre of X-ray Diffraction Studies, Centre for Geo-Environmental Research and Modelling (GEOMODEL) and Innovate Technologies of Composite Nanomaterials (St. Petersburg State University).

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Synthesis and Structure of Hypervalent Antimony Trichloride Complexes with Pyridine

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Stability of hypervalent compounds changes nonlinear with amount of electrons in outer shell. Compounds with 10 electrons in outer shell are rare and very unstable [1]. In contrast, those with 12 electrons in outer shell are more stable and occur more often [2,3].

It is expected that complexes of antimony trichloride with pyridine also should exist in the form of molecules with 12 electrons in outer shell.

Two complexes were synthesized by direct reaction between antimony trichloride and pyridine in vacuum and structurally characterized by X-ray analysis – $\text{SbCl}_3 \cdot \text{Py}$ (**1**) and $3\text{SbCl}_3 \cdot 5\text{Py}$ (**2**). Formation enthalpies of gaseous molecules $\text{SbCl}_3 \cdot \text{Py}_n$ ($n=1-3$) and $\text{Sb}_2\text{Cl}_6 \cdot \text{Py}_2$ were estimated by quantum chemistry calculations (B3LYP/def2svp). Dimerization of $\text{SbCl}_3 \cdot \text{Py}$ into $\text{Sb}_2\text{Cl}_6 \cdot \text{Py}_2$ in gas phase is exothermic, which suggest that dimeric structures may be realized in the solid state. Similar complexes with phosphines exist in the solid state as dimers with 12 electrons in outer shell [2].

Complexes **1** and **2** adopt different structures in the crystal. **1** forms tetramer molecules with 12 electrons in outer shell. Structure of **2** is very rare, because it consists of different molecules. Each unit cell of **2** contains four $\text{SbCl}_3 \cdot \text{Py}_2$ and two $\text{SbCl}_3 \cdot \text{Py}$ molecules. Molecule $\text{SbCl}_3 \cdot \text{Py}$, which formally contains 10 electrons in outer shell, in solid state adopts an additional contact with neighboring $\text{SbCl}_3 \cdot \text{Py}_2$. It supposes that antimony atom in $\text{SbCl}_3 \cdot \text{Py}$ essentially adopts 12 electrons in outer shell in crystal structure of **2**.

We thank SPbU Resource Center “Computing center SPbU” for computational time and A. Virovets and E. Peresyphina (University of Regensburg, Germany) for x-ray analysis.

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Formation of Hydrogel Supermacroporous Matrices for Biomedical Application

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Cryogels are classified as new generation of adsorbents because of their excellent structural properties and flow dynamics [1]. They can be synthesized via free radical polymerization or crosslinking reaction of ready polymer under partially frozen monomer solutions. During the polymerization called as cryogelation, solvent molecules forming solid phase act as porogen to create interconnected flow channels which allow the users to study at high flow rate without any plugging and diffusion problems. In addition, the freezing increases the monomer concentration known as cryo-concentration in unfrozen organic phase which allows obtaining highly cross-linked polymeric network. Water is generally used as solvent in order to synthesize and water-soluble monomers are converted into cryogel forms due to the structural properties of ice crystals. Besides macroporous structure and excellent flow-dynamics, cryogels show good mechanical, chemical, and physical stability. The combination of those properties make the cryogels a promising stationary phase for diverse applications in the several research disciplines including chemistry, medicine, biotechnology, environmental sciences, and food safety [2], [3]. Thus, the aim of this work was to obtain supermacroporous matrices. Cryogels were prepared by copolymerization of 2-hydroxyethyl methacrylate with a functional co-monomer N,N'-methylene-bis-acrylamide or sodium alginate adduct with 2-hydroxyethyl methacrylate and poly(ethylene glycol) dimethacrylate at different co-monomer concentrations and with various crosslinking degrees. The properties of the synthesized systems were studied. Developed interporous connectivity was studied by X-ray nano-tomography method, a presence of large sized (10 - 160 nm) pores in the cryogels was established by SEM method, using uniaxial compression tests resistance to mechanical deformation was investigated. Swelling capacity of obtained cryogels also was studied.

Acknowledgements. The research was supported by Russian Scientific Foundation (# 14-13-00940).

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Peculiarities of Biodiesel Synthesis on the Base of the Model System: Oleic Acid – Ethanol/Methanol- Ethyl Oleate/Methyl Oleate - Water

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Today the trends in the development of modern technologies assume the use of "clean" energy (biodiesel) produced from renewable sources. Biodiesel has several advantages in comparison with fossil sources of energy: it's based on renewable feedstock, non-toxic, biologically degradable and possesses the best lubricating properties [1]. The basis of the biodiesel synthesis process is the esterification reaction of fatty acid with ethyl/methyl alcohol in the presence of a homogeneous acid or alkaline catalyst. Specificity of improvement of the process of biodiesel production is primarily associated with very limited experimental data on the physicochemical and thermodynamic properties of the fatty acid esters. This knowledge is the foundation of any chemical-technological process. There are only isolated literature data [2] for a number of organic acids with long alkyl substituent C10-C12. These results are not reliable source of the data in the application to the process of biodiesel synthesis.

The main research objects are systems with the esterification reactions of ethyl alcohol with oleic acid and methyl alcohol with oleic acid. This work presents the peculiarities of ethyl oleate and methyl oleate synthesis (Fig. 1).

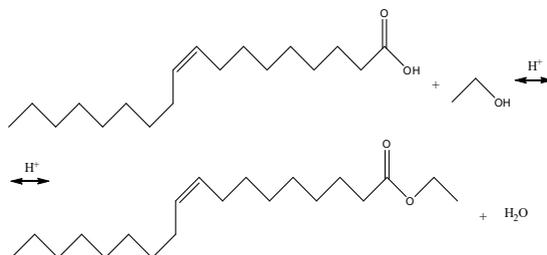


Fig. 1. The esterification reaction of oleic acid with ethanol.

Acknowledgements. The research is supported by the Russian President's Scholarships (SP-2140.2016.1).

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Influence of Two Type of Nucleating Agents on Morphology and Optical Properties of Vanadium Dioxide Nanoparticles

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Vanadium dioxide is a promising material for smart window due to semiconductor-metal phase transition (SMPT) at 68°C. Above this temperature VO₂ is a metal with a tetragonal crystal structure which does not skip IR radiation, but below it is a monoclinic transparent semiconductor. The IR transmittance (T) value and SMPT intensity depend on a structure of VO₂ and size of nanoparticles [1]. It is known that the structure and the size of inorganic oxides could be regulated using the nucleating agents with the given phase composition. To the best of our knowledge, there are no works dedicated to the impact of nucleating agents on VO₂ morphology and functional properties.

The aim of this work was to obtain vanadium dioxide in presence of SnO₂ (tetragonal structure) and CuO (monoclinic structure) with the amount from 1 to 20%, as well as to study their infrared transmittance at different temperatures.

VO₂ were obtained by hydrothermal synthesis, the nanoparticles morphology and properties were examined using X-ray diffraction (XRD), scanning electron microscopy (SEM), dynamic light scattering (DLS), SSA estimation (BET method) and IR-spectroscopy.

It was found that the powders containing 5 and 10% of nucleating agents are optimal in terms of phase composition, size and shape of nanoparticles. The IR transmittance spectra of the coatings on glasses based thereon demonstrated the difference of T values for semiconductor and metal phase. The best result was found for the sample with 10% of monoclinic CuO.

Acknowledgements. The authors are grateful to the RFBR grant № 16-03-00167-a and Resource Centers of the Research Park of St. Petersburg State University: Centre for Geo-Environmental Research and Modelling (GEOMODEL), Centre for X-ray Diffraction Studies, Chemical Analysis and Materials Research Centre, Center for Innovative Technologies of Composite Nanomaterials.

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Synthesis of Amphiphilic Block-Copolymers with Terminal Fluorescent Labels

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With intensity development the laser scattering confocal microscopy, the research methods of biological object based on fluorescence, has come to be actively used in biomedical chemistry [1]. For example, it has become possible to study the dynamics and function of biological macromolecules, to investigate the chemical composition of living cells. Furthermore, due to the growing interest in this field and accessibility of the method give rise to appearance such self-direction as fluorescence molecular imaging. This method is indispensable in experimental oncology. In the recent years research directional on uses of fluorescent nanoparticles as an agents for the visualization of a cellular-process.

The purpose of this work was prepared nanoparticles formed by polyamino

acids with terminal fluorescent labels and study their interaction with the cells. Synthesis of block-copolymer was based on ring-opening

p o l y m e r i z a t i o n
N-carboxyanhydrides of L-Lysine and L-Leucine [2]. Cysteine platinum complex was used as initiator,

which thanks to fluorescent properties allows to detect the penetration of the particles in the cell (was used the cell line U-937 - oncogenic human monocyte). Visualization of this process was carried out by confocal laser scanning microscopy. Description intermediates bring about of physical and chemical methods of analysis, the ratio of hydrophilic and hydrophobic blocks - gel permeation chromatography and chromatographic amino acids analysis. According to the data of confocal microscope, the size of nanoparticles is less than 700 nm.

Acknowledgements. This work was supported by the Russian Science Foundation (№ 14-50-00069).

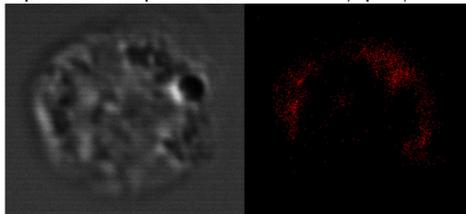


Fig. 1. Interaction nanoparticles formed by poly(L-Lysine)-block-poly(L-Leucine) copolymer with the cell; from left to right - microscopy in transmitted light and fluorescence microscopy.

monocyte). Visualization of this process was carried out by confocal laser scanning microscopy. Description intermediates bring about of physical and chemical methods of analysis, the ratio of hydrophilic and hydrophobic blocks - gel permeation chromatography and chromatographic amino acids analysis. According to the data of confocal microscope, the size of nanoparticles is less than 700 nm.

Acknowledgements. This work was supported by the Russian Science Foundation (№ 14-50-00069).

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Second Harmonic Generation in 2d Coordination Polymer

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After appearing in the scientific world a new class of compounds called metal-organic frameworks and coordination polymers, the rapid study of the synthesis of the new features of this species was begun. However, despite of the full range of existing techniques, the receiving of new materials with specific properties was rather complicated question. One way to overcome existing disadvantages of the synthesis of metal-organic frameworks and coordination polymers is to use a method of growing crystals in a slow diffusion conditions. Thus it was produced a new compound of coordination polymer based on copper ions.

The resulting crystals are transparent in the visible region, and in turn have a high efficiency in the second harmonic generation, comparable to the commercially used materials, despite the fact that the obtained crystals are thin enough. Moreover, the resulting material does not undergo degradation when exposed to laser radiation and is stable in air. Thus, the prospect of obtaining the new compound which can be used in the field of nonlinear optics is shown. The properties of this material can compete with the organic films and commonly used organic crystals.

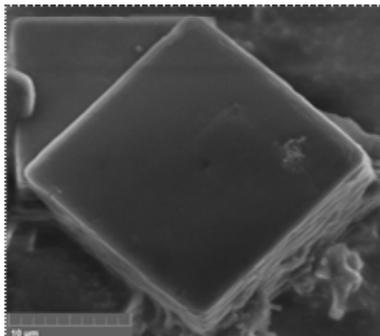


Fig. 1. Microphotography of coordination polymer obtained by scanning electron microscopy.

A Study of the Protonation and Hydration of Layered Perovskite Bismuth Titanates

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Perovskite-like oxides are complex oxides that consist of alternating perovskite blocks $[A_{n-1}B_nO_{3n+1}]$ and layers of different structures. Layered perovskites have been widely studied as perspective ionic conductors, ferroelectric materials and photocatalysts [1]. In recent years their ability to undergo topochemical reactions and ionic exchange attracts increasing attention. [2] In special cases the intercalation of water and organic molecules into interlayer space is possible, which determines the higher photocatalytic activity of layered oxides compared to non-layered structures. The most studied phases of layered perovskites are: Ruddlesden-popper (RP) $A_2[A_{n-1}B_nO_{3n+1}]$, Dion-Jacobson (DJ) $A[A_{n-1}B_nO_{3n+1}]$ and Aurivillius $[Bi_2O_2][A_{n-1}B_nO_{3n+1}]$ phases.

The present research considers ability of Bismuth-containing complex oxides: $CsBi_3Ti_4O_{13}$ (DJ), $K_{2.5}Bi_{2.5}Ti_4O_{13}$ (RP) and $Bi_4Ti_3O_{12}$ (Aurivillius) to undergo protonation and intercalation of water molecules into interlayer space. Under certain conditions of nitric acid treatment the formation of nitro derivatives was observed.

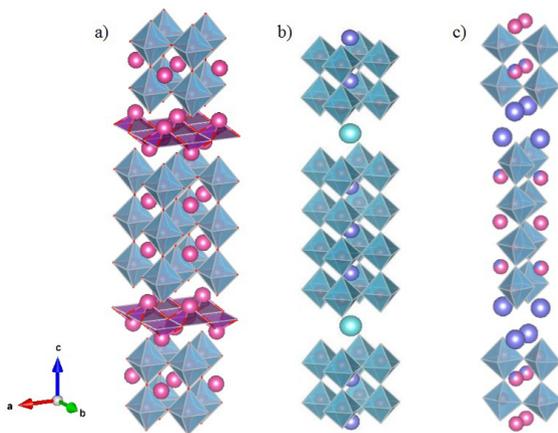


Fig. 1. Structures of a) $Bi_4Ti_3O_{12}$; b) $CsBi_3Ti_4O_{13}$; c) $K_{2.5}Bi_{2.5}Ti_4O_{13}$.

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Application of Green Chemical Principles to the Synthesis of CdSe Quantum Dots

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Over the past decades, semiconductor quantum dots, especially CdSe quantum dots, which exhibit excellent size-tunable optical properties and soluble characteristics, have drawn great attention both in fundamental researches and practical applications [1].

In most articles, CdSe QDs have been synthesized at temperatures above 200 °C using trioctylphosphine oxide (TOPO) as solvent and trioctylphosphine (TOP) as capping agent which are hazardous in nature.

We have developed a much cheaper and greener route to monodisperse CdSe quantum dots with wurtzite structure. The hexadecane was chosen as the solvent, eliminating the needs of air-sensitive and toxic TOP, and cadmium oxide or cadmium acetate and elemental selenium as sources. We have carried out a systematic integrated approach to the study of the synthesis process of cadmium selenide nanoparticles under conditions when the reactants appear in solution for the determination of the formation mechanism of quantum dots and its dependence on varying the synthesis parameters: cadmium precursor, fatty acid and temperature.

The crystal structure of the as-synthesized product was analyzed by XRD with CuK α radiation. The optical characteristics of obtained nanocrystals are traced by measuring the absorbance fluorescence spectra of the aliquots.

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From Easily Available Hetarylpyrroles to Novel Heterocyclic Frameworks

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Luminescent materials are the basis for a wide range of modern technologies such as sensing, organic light emitting diodes (OLEDs), nonlinear optics, various techniques in bioimaging and phototherapy. Fused heteroaromatic molecules frequently possess luminescent properties. Recently we have developed an approach to new heteroaromatic framework **A** (Fig. 1) with outstanding fluorescent properties [1]. DFT calculations predict that compound **B** also may have valuable luminescent features.

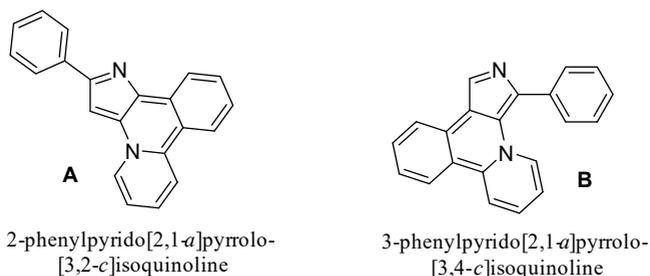
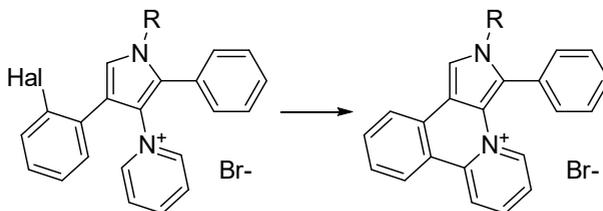


Fig. 1. Novel heterocyclic frameworks.

The key stage for the synthesis of heteroaromatic skeletons **A** and **B** (Fig. 2) is an intramolecular arylation. For compound **A** it was achieved through cyclization on Pd(II) but this approach failed in the case of compound **B**. The alternative way – radical cyclization – has been investigated.



*Fig. 2. Key stage for the synthesis of heteroaromatic skeleton **B**.*

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Automated Electrochemical Determination of Hydrogen Sulfide, Methanethiol and Ethanethiol in Crude Oil and Biodiesel with On-Line Chromato-Membrane Extraction

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Determination of hydrogen sulfide, methanethiol and ethanethiol in crude oil and biodiesel is an important task in quality control of both crude oil and biodiesel, because these compounds are of acid nature and therefore, they can provoke corrosion in the oil refining equipment. Currently, gas chromatography is used to determine hydrogen sulfide, methanethiol and ethanethiol in crude oil. However, in this case, we have to calibrate the gas chromatograph with standard gas mixtures of analytes and this limits the use of the method.

Alternatively, in this work we propose a new, fully automated sample preparation method for electrochemical determination of hydrogen sulfide, methane- and ethanethiol. The method includes the formation of **volatile analytes and their subsequent** absorption into chromatomembrane cell. The detection of analytes occurs in a special three electrode flow-through cell. In order to separate sulfide, methanethiol and ethanethiol we propose using different absorption solutions, such as sodium carbonate for sulphide ions, and sodium hydroxide for methane- and ethanethiol.

The developed method was used for the quantitative determination of hydrogen sulfide, methane- and ethanethiol in the crude oil samples and biodiesel.

Development of a Conjugate for 5-hydroxy-8H-chromeno[2',3':4,5]imidazo[2,1-a]isoquinoline

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One area of study on department of Organic Chemistry RUDN is domino-modification of isoquinolines. 5-Hydroxy-8H-chromeno[2',3':4,5]imidazo[2,1-a]isoquinoline (Fig. 1) was obtained by the base-catalyzed reaction of isoquinolinium salts with salicylic aldehyde [1]. Because of the imidazo fragment, chromenoimidazoisoquinolines may have anticancer activity.

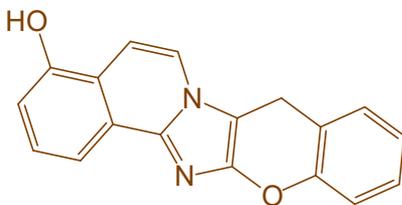


Fig. 1. 5-Hydroxy-8H-chromeno[2',3':4,5]imidazo[2,1-a]isoquinoline (HCII)

It was decided to combine HCII with a peptide linker. The precursor EMC-Phe-Lys-PABC-HCII (Fig. 2) has been successfully synthesized.

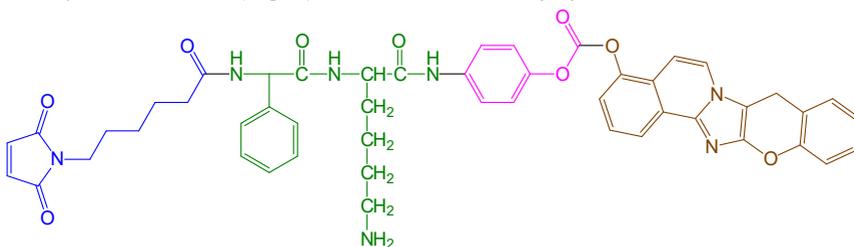


Fig. 2. EMC-Phe-Lys-PABC-HCII.

This makes it possible to attach a linker to polymer supports, such as polyglycerol. Suitable polymer-based drug delivery systems can enable controlled release and specific delivery of bioactive agents to the diseased or damaged tissue (by non-covalent or covalent attachments) [2].

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Preparation and Properties Investigation of Flow-through Heterogeneous Biocatalysts based on Macroporous Monolithic Materials

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Today enzymatic processes are widely used in various fields of industry and science [1]. However, usage of soluble enzymes has a number of disadvantages such as high cost of enzymes and necessity of biocatalyst recovery after reaction under conditions saving its activity. The immobilization of enzyme, namely, its binding to a solid support, represents the way that allows overcoming these limitations. Protein fixing helps to stabilize its conformation, prevent denaturation and decrease of its catalytic activity, simplification of biocatalyst removal as well as possibility of enzyme reuse [2]. Macroporous monoliths are characterized by unique structure allowing the realization convection controlled mass transfer at high flow rates of a mobile phase [3].

The aim of submitted work was a development of the effective flow-through heterogeneous biocatalysts consisting of ribonuclease A immobilized on macroporous monolithic stationary phases and exploration of properties of the prepared bioreactors.

In this study macroporous polymethacrylate monolithic columns with different pore size were synthesized and used as stationary phases for ribonuclease A immobilization. An enzyme immobilization was carried out through the intermediate polymer spacer providing the distance of the biocatalyst from the solid surface. Studying of properties of prepared biocatalysts was carried out by recirculation mode using a specific low-molecular weight substrate (cytidine-(2')3'-cyclophosphate). The high efficiency of the obtained heterogeneous biocatalysts comparable to catalytic reaction in solution was demonstrated. Moreover, the dependence of catalytic properties of heterogeneous biocatalysts from porous characteristics of the solid support was established.

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Synthesis of Colloidal CdSe Quantum Dots: Safer, Cheaper and Faster

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Semiconductor nanoparticles exhibit exciting size-tunable optical, magnetic, chemical and electronic properties with practical applications in a wide spectrum of fields including catalysis, photonics, photovoltaics, electronics, biological imaging and data storage [1].

Colloidal approaches provide quantum dots of excellent quality due to the control in their size, shape, structure and composition of the material, and hence can be directly used for the respective applications.

The widespread way of synthesis of CdSe QDs consists in course of reaction at temperatures above 200 °C using trioctylphosphine oxide (TOPO) as solvent and trioctylphosphine (TOP) as capping agent, which are hazardous in nature.

We have developed a much cheaper and green Non-TOPO/TOP-Based synthetic route of a series of CdSe QDs in the high boiling point solvents by injection of Se powder into a Cd oleic acid solution without use of TOP. N-hexadecane was selected as the solvent. It is cheaper, environmentally friendlier, and more stable in the atmosphere than the reported solvents such as TOPO or ODE.

The CdSe quantum dots have been successfully synthesized in the temperature range 230-260°C (with a step of 10 degrees). The increase in particle size with red shift in colour was also confirmed by the UV–Vis absorption spectra. Ultraviolet and visible absorption spectra were recorded at room temperature. Photoluminescence spectra were measured and the photoluminescence quantum yield was obtained. X-ray powder diffraction analysis was employed. To further clarify the particle size of CdSe QDs we used transmission electron microscopy and dynamic light scattering.

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Preparation of Titanium Oxide and Calcium Phosphate Based Coatings by Sol-Gel Method and Investigation of their Structural Characteristics

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Currently, one of the main problems of orthopedics and dentistry is the creation of the implants with improved biocompatible and bioactive properties. For this purpose, it was found that the chemical composition and the structure of the implant surface are of great importance [1].

As titanium dioxide proved itself as good biomedical coating [2], in our research we have developed a synthesis of TiO_2 films with different morphologies on the surface of the titanium substrate by dip-coating.

This method is based on creating coatings on the flat surface by using the sol-gel process (Fig. 1). In this work the formation of the defects on the TiO_2 xerogel films have been investigated. By varying the synthesis conditions, we managed to get coatings with different microstructure (such as network structure, and the structure, which consists of through cracks to the surface of titanium).

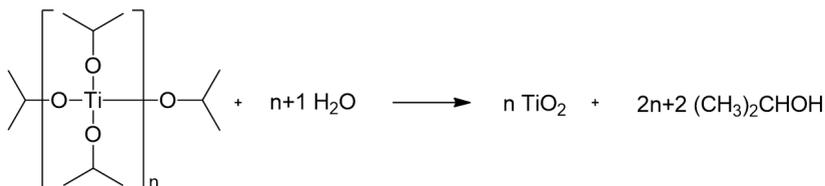


Fig. 1. The synthesis of TiO_2 .

As a result, we obtained the coatings with complicated organization of the surface at the micro- and nanoscale, which showed high adhesion properties of osteoblastic cells. These nano-coatings with controlled surface structure are of practical interest in the future in the field of medical implants with improved bioactive properties.

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The Influence of Different Stabilizers on the Formation of Alginate Nanoparticles

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Recent advances in nanotechnology have encouraged researchers to produce nanoscale materials. A major area of work in this regard has been to obtain polymeric nanoparticles for enzyme-triggered drug release [1, 2]. For instance, calcium-alginate hydrogel nanoparticles have been widely used in a variety of drug delivery systems, because of their biocompatibility, biodegradability and non-toxicity [2]. There are a number of independent works on alginate nanoparticles synthesis carried out at different conditions (cross-linking agent, stabilizer, etc.). However, to the best of our knowledge, no study has yet demonstrated the interaction between a certain parameter and properties of obtained particles.

The present study was aimed to investigate the influence of different stabilizers on alginate nanoparticles formation. Five stabilizers of different nature (PVA, SDS, CTAB, lecithin, oleic acid) were used in various concentrations (0.5-5 %) and proportions to deduce their impact on the process. It was shown that PVA (1%, 5%) and SDS (1%, 5%) encouraged the formation of particles with the diameters range from 500 to 1000 nm, meanwhile other stabilizers and their mixtures led to polymeric film formation. Moreover, the procedure of synthesis (duration, conditions, solvent, etc.) played a very important role as well. Nevertheless, the research is still in progress and results are under discussion.

Acknowledgements. Scientific researches were performed at the Centre for Geo-Environmental Research and Modelling, Centre of X-ray Diffraction Studies, Centre for Optical and Laser Materials Research and Chemical Analysis and Materials Research Centre of St. Petersburg State University.

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Synthesis and Characterization of the First Example of Cyclometalated Palladium(II) Complex with ADC-Ligand

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In the last decade, palladium complexes with acyclic diaminocarbene (ADC) ligands attracted great attention as catalysts for different organic transformations. The metal-mediated coupling of palladium(II)-isocyanides with nitrogen nucleophiles is one of the most efficient and versatile method for generation of palladium(II) ADC complexes. On the other hand, the tuning of ligand environment allows widely change structure and properties of palladium diaminocarbene complexes.

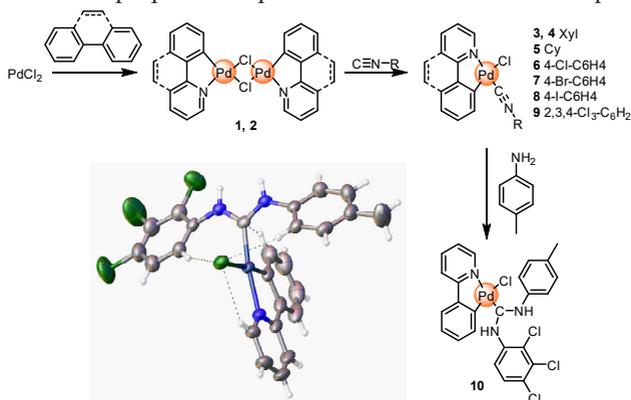


Fig. 1. Synthesis of cyclometalated palladium(II) complexes.

We have synthesized previously not described palladium isocyanide complexes cyclometalated by phenylpyridine and benzoquinoline **3–9**. Only complex **9** enters in the reaction with a nucleophile (*p*-toluidine) giving a first example of cyclometalated palladium(II) complex with ACD ligand **10** (Fig. 1).

Pure complexes **3–10** were characterized by high resolution ESI⁺-MS, FTIR, 1D (¹H, ¹³C{¹H}) and 2D (¹H, ¹H-COSY, ¹H, ¹H-NOESY, ¹H, ¹³C-HSQC, ¹H, ¹³C- and ¹H, ¹⁵N-HMBC) NMR spectroscopies. In addition, the solid state structures **4–10** were elucidated by single-crystal X-ray diffraction.

Acknowledgements. This work was supported by RFBR (grant 14-03-00297) and government of RF (grant of President of RF MK-7425.2016.3). Physicochemical studies 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 SPbU).

Organic Acids as Morphology and Functional Properties Regulation Agents for VO₂ Nanoparticles

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Vanadium dioxide is one of the most perspective material due to its functional properties. Firstly, it undergoes a semiconductor-to-metal phase transition (SMPT) at 68°C. At this temperature magnetic, electrical and optical properties of VO₂ change abruptly so it can be used as a material for thermosensors, thermoswitchers and smart coatings for windows. Also crystal structure of VO₂ is able to intercalate Li and Al ions reversibly. Therefore, the oxide is promising for electrodes in Li/Al-ion batteries.

Functional properties of vanadium dioxide depend on its morphology and crystal structure [1]. Control of particle's size, shape and structure will lead to SMPT temperature decrease to required interval and increase of discharge capacity and cycle stability.

In this work such organic acids as oxyethylidenediphosphonic, tartaric, succinic and salicylic are used as morphology regulation agents in hydrothermal synthesis of VO₂ nanoparticles.

Morphology and surface composition are investigated by X-ray diffraction, scanning electron microscopy and IR spectroscopy. Specific surface area of the powders is determined by BET method.

Three different types of VO₂ morphology are obtained: rods, spheres and carmbolas. It is shown that different influence of organic acid is caused by inequality of dissociated OH-groups.

Application of obtained samples for Li-ion batteries is successfully performed. It is observed that the discharge capacity of electrode made of VO₂-rods is three times higher than of the one made of VO₂-spheres. Its cycle stability has the same tendency.

Acknowledgements. This work is supported by RFBR grant № 16-03-00167-a. Investigations are carried out in Resource Centers of the Research Park of St. Petersburg State University: Centre for Geo-Environmental Research and Modelling (GEOMODEL), Centre for X-ray Diffraction Studies, Chemical Analysis and Materials Research Centre. Authors thank Dr. O.V. Levin and E.V. Alekseeva for their contribution in electrochemical part of the experiments.

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Towards Optical Sensing of Individual Ion Activity: the Role of Organic Salts in Polymeric Ion-Selective Optodes

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Ion-selective optical sensors (optodes) are widely used in various fields of science and industry. Just as for the ion-selective electrodes, their signal is the result of electrochemical processes such as an ion-exchange between the optode phase and the solution. However, their signal, in full analogy with the galvanic cell without liquid junction, is dependent on either ratio or product of the two ion activities – of the analyte ion and the reference ion.

The general concept for the optical sensing of individual ion activity was suggested in [1], where it was shown that the single ion optodes are similar to the galvanic cell with liquid junction. According to the developed model, the Galvani-potential on the phase boundary between the optode and the solution must be stabilized. It was achieved by adding lipophilic organic electrolyte to the optode membrane. Its distribution between the phases was shown to stabilize the Galvani-potential.

In this contribution we studied how the response of the single ion-sensing optode depends on the optode membrane composition. pH/Na-selective optode was chosen as a sample system, H^+ being the analyte ion, and Na^+ a reference ion. The response curves were obtained for several optode compositions with different concentrations of the active lipophilic components (Fig. 1). A strong dependence of the response range and span on the quantitative composition of the sensor was observed. The effects of the components nature, organic salt nature and the polarity of the plasticizer were studied as well. All the optodes under study demonstrated negligible dependence of their pH-response on Na^+ content in the contacting solution. Thus, by changing the optode membrane composition one can adjust the sensitivity range of the sensor to the range of interest keeping its response independent on the reference ion activity.

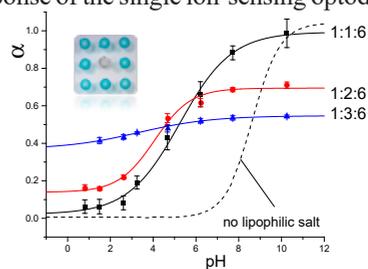


Fig. 1. Response of the single-ion optodes of different composition. The numbers: molar ratios of the chromoionophore to organic salt to sodium ionophore. Inset: the optode array.

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Synthesis and Structure of Complexes of Antimony Tribromide with Pyridine

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Donor-acceptor complexes play an important role in biological systems, they are widely used in various industries, medicine. Also, they are promising precursors for the synthesis of high-purity solid materials by chemical vapor deposition (CVD) [1]. Recently structurally characterized InBr_3Py_x complexes ($x = 1-3$) have been reported [2]. Unexpectedly, the complex with $x = 2$ exists as molecular dimer $\text{In}_2\text{Br}_6\text{Py}_4$ which features a planar In_2Br_6 unit with 12-electron valence shell for the indium atoms. Quantum chemical computations predicted the existence of the valence-isoelectronic $\text{Sb}_2\text{Br}_6\text{Py}_2$ dimeric complex.

In the present work we report about the synthesis of the complexes of antimony tribromide with pyridine with a wide range of ratio of components. Due to the high sensitivity of SbBr_3 and its complexes to moisture, all operations were performed in a sealed whole glass apparatus under vacuum. The complexes have been prepared by direct interaction between components.

Crystal structures of SbBr_3Py_x complexes have been determined by single crystal structure analysis. For $x = 1$ the complex actually do adopts a dimeric structure $\text{Sb}_2\text{Br}_6\text{Py}_2$ with octahedral environment on the Sb atom. The complex with $x = 2$ exists as a SbBr_3Py_2 monomer where the central atom has an pseudo-octahedral environment. The complex SbBr_3Py_3 is unstable due to losing one pyridine ligand. Interestingly, when starting ratio of the $\text{SbBr}_3:\text{Py}$ is 1:1.5 two different compounds were co-crystallized in one unit cell: $\text{Sb}_4\text{Br}_{12}\text{Py}_6$ and $\text{Sb}_8\text{Br}_{24}\text{Py}_{13}$. Moreover, the $\text{Sb}_4\text{Br}_{12}\text{Py}_6$ exists in two different isomeric forms.

Acknowledgements. We are grateful to A.V. Virovets and E.V. Peresyphkina (University of Regensburg) for the X-ray structure determination.

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Optical Properties of Er³⁺ Doped Sulfide Glasses

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Chalcogenide glasses doped with lanthanides ions attract attention due to the combination of several unique properties which provides high luminescence efficiency and makes them attractive materials for lasers and optical devices [1].

The purpose of the present work was to receive additional information about the interconnection between the spectral properties of erbium ions in glass matrix and the glass structure including specialties of Er³⁺ ions embedding to the glass lattice.

The absorption and luminescence spectra of the chalcogenide glasses in the (1-x)[0.15Ga₂S₃·0.85GeS₂] system have been investigated. The X-Ray diffraction analysis was carried out. The increase of erbium absorption band wavelength with the growth of lanthanide concentration indicates a decrease of erbium ion effective charge. At the same time insignificant change of the first sharp diffraction peak angular position points out the invariability of the medium-range order correlation length. The probability of definition of the dependence of the luminescence intensity on the rare-earth dopants concentration using the previously proposed equation [2] is discussed.

Acknowledgements. All measurements were carried out at the Centre for optical and laser materials research and Centre for X-Ray diffraction studies of Saint-Petersburg State University.

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Atomic Emission Spectral Determination of Micro- and Macro Elements in Commercial Fruit Juices

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Nowadays juices are an inalienable part of human ration. They include a large amount of elements that are essential for the human's health and provide the possibility for normal organism functioning. However, some toxic elements can appear in juices due fruits growth on contaminated area of low-grade production. In addition, essential elements have a threshold limit value. This is the reason to control their concentrations in drinks that people consume every day.

The problem of element concentration determination is being widely investigated all over the world. Therefore, nowadays many methods exist. Although all of these methods provide good accuracy, they usually include sample mineralization step that extend the time of analysis and involves using of many additional reagents that increase the probability of an error. Thus, the qualitative analysis with no preliminary sample mineralization of commercial juices is the aim of this research.

The qualitative analysis with no preliminary sample mineralization of commercial apple, cherry and orange juices for the determination of micro- and macro elements was made using arc atomic emission spectrometry with dried residue. Report presents the results of choosing necessary amount of a sample, allowing to determine elements without matrix influence and to avoid formation of sugar film at the top of electrode. In addition, flame emission spectroscopy for the determination of alkaline metals was used. Results of selection of sufficient sample dilution and appropriate spectral buffer for the elimination of matrix influence are also shown. Checking of accuracy was carried out by addition method.

Acknowledgements. Part of the research was done using the equipment of the Educational Resource Center of Chemistry of Research Park of St. Petersburg State University.

Gas Separation Performance of Novel Mixed Matrix Membranes Based on Star-Shaped Macromolecule

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In recent years, mixed matrix membranes (MMMs) have been extensively used in the gas separation process due to good mechanical, chemical and thermal stability as well as high permeability and selectivity in comparison to nonmodified polymer membranes. The MMMs, which are prepared by incorporating inorganic materials as dispersed phase into the polymer matrix, have the advantages of both inorganic and polymeric materials. To obtain good adhesion between two phases is the most important task for MMMs production. In the present work, a new type of star-shaped macromolecule containing small C_{60} core and 6 arms of polystyrene (FPS) has been used to prepare MMMs.

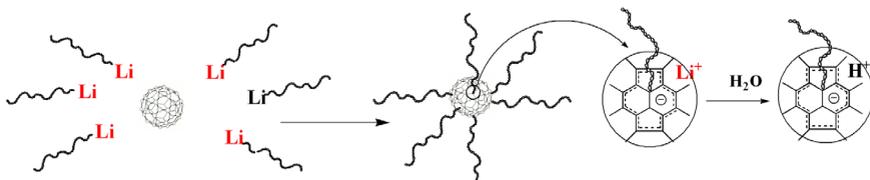


Fig. 1 Reaction of the polystyryllithium with C_{60} gives FPS.

Membranes based on MMMs were characterized by scanning electron microscopy, thermogravimetric analysis, determination of density and contact angle analysis.

Gas separation tests were carried out by using a laboratory high vacuum apparatus with a static permeation cell for a number of pure gases: H_2 , O_2 , N_2 , CH_4 . Gas transport properties of all novel membranes were compared with the data of separation properties of known membranes by using Robeson's diagram. It was established that membranes containing FPS are more effective as nonmodified polymer film.

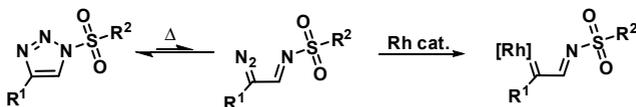
Acknowledgments: This work was supported by Fellowship of the President of Russian Federation (project № 184, SP-1469.2015.1) and St. Petersburg State University (event 6, project № 12.42.1452.2015). Equipment of Resource Centers of St. Petersburg State University, namely "Thermogravimetric and calorimetric methods of investigation", "Chemical Analysis and Materials Research Centre", Interdisciplinary Resource Center "Nanotechnologies" and Education Resource Centre in the direction of chemistry were used for membrane investigation.

Rh(II)-Catalyzed Reactions of 1-Sulfonyl-1,2,3-Triazoles with 5-Alkoxyisoxazoles

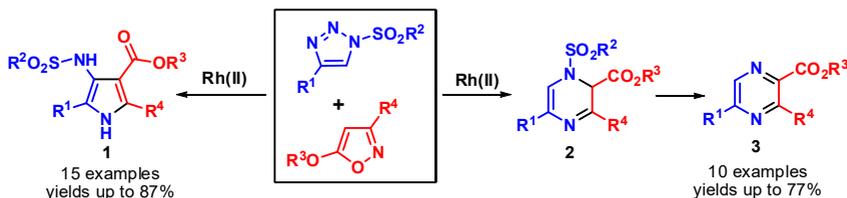
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1-Sulfonyl-1,2,3-triazoles are widely used in organic synthesis as starting materials for the construction of various carbocyclic and heterocyclic compounds. An important feature of such systems is their ability to exist in equilibrium with their open-chain form – diazoimines in solution while heating. This process finds application in generation of such reactive species as rhodium azavinyl carbenes [1, 2].



In present work the reaction of 5-alkoxyisoxazoles with rhodium carbenoids generated from 1-sulfonyl-1,2,3-triazoles have been investigated. The reaction leads to the mixture of two isomeric products, 3-aminopyrrole **1** and 1,2-dihydropyrazine **2**. The ratio of these products strongly depends on the reaction conditions. Proper selection of such parameters as ligands in rhodium catalyst, temperature and solvent allows to direct the reaction towards the formation of one of the desired products and obtain it in good yield. Conditions for the transformation of unstable 1,2-dihydropyrazines **2** into stable pyrazines **3** have been found. Moreover, it was determined that this reaction can be realized also for less reactive 5-phenylisoxazoles. Thus, presented reaction can be a convenient method for the synthesis of highly functionalized pyrrole and pyrazine derivatives.



This work includes a detailed study of the influence of substituents' nature on the ratio of products as well as quantum-chemical investigation of the mechanism for its formation.

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Simultaneous Phase and Chemical Equilibrium in Systems with Liquid Phase Splitting under Polythermal Conditions

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Currently available theoretical and experimental data on liquid-phase multicomponent systems with chemical reaction is limited. The study combined reactive mass transfer processes, in which both implemented chemical and phase equilibrium, leading to the establishment of new physical and chemical regularities. The main task is thermodynamic analysis of the features of liquid-liquid (LL) phase diagrams of the systems with equilibrium and non-equilibrium chemical reaction in solution. This research has not only fundamental, but also the practical importance of the problem of liquid phase splitting of reaction mixtures; this effect fundamentally changes the technological process of chemical synthesis.

The object of investigation in this research is quaternary reacting system propionic acid - ethanol - ethyl propionate – water. The ternary and binary subsystems were studied.

To study the solubility in stratified system was used isothermal titration method. The experimental data on the solubility was obtained for binary, ternary and quaternary systems at a temperature of 20, 30 and 40 °C. On the base of the experimental data of the solubility in the system investigated the solubility surface was constructed in concentration tetrahedron.

Chemical equilibrium was studied at 20, 30 and 40 °C. The experimental data on chemical equilibrium in system investigated was obtained by two different methods: the classical method of gas chromatography and relatively new one for this theme – by nuclear magnetic resonance method. The surfaces of chemical equilibrium were obtained by gas chromatographic method analysis at 20 °C, method of NMR – at 30 and 40 °C.

For the first time was found the intersection of the solubility surface and chemical equilibrium surface in the concentration area. Data were obtained on the simultaneous phase and chemical equilibrium and constructed the intersection of these surfaces at 30 and 40 °C. For clarity, results were presented in the concentration square of transformed variables.

Acknowledgements. The authors also acknowledge Resource Center SPbGU "Magnetic Resonance Research Centre". The research is supported by the Russian President's Scholarships (SP-2140.2016.1).

The Effect of Background Salts on Copolymers of Diallyldimethylammonium Chloride and 2-(diallyl(methyl)ammonio)acetate in Solution

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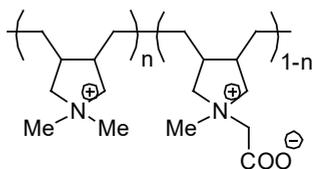
The polyelectrolytes based on copolymers of N,N-diallylammonium salts are widely applied as antistatic agents, rheology modifiers, coagulants and a base for ion-exchange resins [1]. The distinctive feature of these polymers is the ionogenic quaternary ammonia groups in the main chain. The anionic fragments present either as free counterions or as pendent groups. The structure of the polyelectrolytes is easily controlled by the variation of substituents and the choice of comonomers.

The polymers demonstrate the hydrolytic stability in the wide range of pH and the high charge density. For these reasons, the copolymers of N,N-diallylammonium salts may serve as promising objects for study.

In solution, the macromolecules' conformation depends both on the charge distribution and on background ions.

In the current report the copolymers of diallyldimethylammonium chloride (DADMAC) and 2-(diallyl(methyl)ammonio)acetate (2-DAMA) differing in composition ($n=0, 0.1, 0.3, 0.5, 0.7, 1$) were prepared by free-radical copolymerization. The influence of different ionic strength and low molecular weight background electrolytes on conformational properties of polyelectrolyte was studied by viscometry and light scattering [2] in the aqueous solutions containing salts with various cations ($\text{Na}^+, \text{Li}^+, \text{Cs}^+, \text{H}^+$) and anions ($\text{Cl}^-, \text{Br}^-, \text{I}^-, \text{ClO}_4^-$). The relationship between intrinsic viscosity $[\eta]$ and the ionic strength of the solution was also investigated for three samples ($n=0, 0.3, 1$). Particular ions that lead to polymer compaction were found.

Acknowledgements. The author is grateful to Resource Centre for Magnetic Resonance SPbSU and for help and advice from colleagues [2].



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Magnetic Proteolytic Nanocomposite

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Proteolytic enzymes find numerous applications in medicine for example for cancer tumors treatment and in cosmetology. One of the most promising members of this class of enzymes is a collagenase due to its narrow specificity in cleavage of collagen - the main structural body protein. However, non-directed application of collagenase can cause a number of side effects, such as nonselective cleavage of the extracellular matrix, which leads to inflammatory reactions and tissue damage. To enhance effectiveness of collagenase and to reduce negative effects systems that will allow specific targeting are needed.

Here we present a new class of magnetically targetable proteolytic systems based on collagenase G enzyme and magnetite nanoparticles. Fully biocompatible nanocomposites are obtained by direct entrapment of Collagenase G molecules into magnetite sol-gel matrix. Entrapped enzyme shows high thermostability, its denaturation temperature is shifted from 61°C to 79°C and temperature of its maximal activity is elevated by 10°C. Nanoarchitecture of the composite doesn't interfere with bioactivity of the entrapped enzyme and it is capable of degrading the gelatin samples, the molecules of collagen and collagenous tissue such as fascia while retaining the constancy of the composition without the release of collagenase molecules from the composite. Due to the synthesis conditions and used materials the composite is fully biocompatible and is suitable for intravenous administration. This class of proteolytic systems opens the door to a new era of medicine - minimally invasive nanodimension operations and can be used in the fight against pathologies associated with collagen diseases, such as adhesive disease and contracture Dupuytren. The work is supported by grant MK-9109.2016.3.

Polynuclear cage-like Au(I) Phosphane Complexes Based on S²⁻ Template; Observation of Multiple Luminescence in Coordinated Polyaromatic Systems

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The polynuclear M(I) complexes of copper subgroup metals containing sulfido and thiolate ligands for decades attract considerable attention due to their ability to form versatile 2D and 3D molecular architecture, which are based on bridging properties of the sulfur coordinating center, templating role of polydentate auxiliary ligands and intra- and intermolecular metallophilic interactions typical for this class of metal compounds.

Rigid diphosphanes containing polyphenylene spacers between phosphorus atoms are suitable template for construction of cage-like complexes [2] and synthetic procedure combining the diphosphane with sulfide ion as another template was expected to give a targeted cage-like structures with interesting photophysical properties. In the present communication we report on the synthesis of a series sulfide-diphosphane polynuclear Au(I) complexes, which display multiple emission including unusual combination of two phosphorescence and one fluorescence bands for a solid state sample of hexanuclear gold complex (Fig. 1).

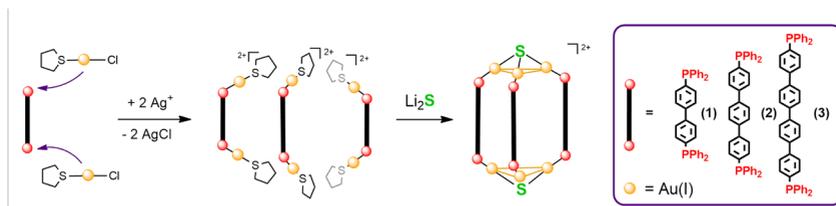


Fig. 1. Scheme of the synthesis of the complexes 1 – 3.

Acknowledgements. This research has been supported by grant of the Russian Foundation for Basic Research 16-33-60109, the Russian Presidential scholarship SP-2534.2016.1

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Solid State Structure of Complex of Ammonia Borane with Tetraglyme

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Molecular complex of ammonia borane with tetraglyme of 2:1 composition was obtained as a side product of CsNH_2BH_3 preparation. According to CCDC database it is the first complex of ammonia borane with acyclic polyether. Structure of complex was determined by single-crystal X-ray diffraction measurements (Fig. 1) and computation methods.

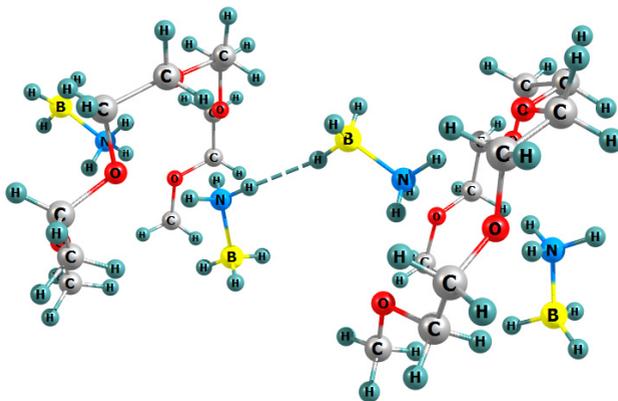


Fig. 1. Molecular structure of $\text{C}_{10}\text{H}_{22}\text{O}_5 \cdot 2\text{BH}_3\text{NH}_3$ in the crystal. Two molecules connected by N-H—H-B dihydrogen bond.

It is interesting to note that there is one short contact (1,94 Å) N-H---B-H (see Fig. 1) between adjacent $\text{C}_{10}\text{H}_{22}\text{O}_5 \cdot 2\text{BH}_3\text{NH}_3$ complex particles. This dihydrogen bonding is found to be shorter comparing with similar interaction in ammonia borane crystals (2.02-2.32 Å) [1].

In present work we compare features of hydrogen bonding in complexes of ammonia borane with crown-ethers and tetraglyme.

Acknowledgements. This work was supported by Science Foundation grant 14-13-0015. We thank Computer Center Resource Center of SPSU for computational time and A. Virovets (University Regensburg) for conducting X-ray diffraction measurements.

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Surface Modification, Characterization and *in vitro* and *in vivo* MRI Studies of Fe₃O₄ Nanoparticles

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At nowadays, one of the most popular methods of earlier diagnostics of different disease is magnetic resonance imaging (MRI) [1]. This method is based on the analysis of the spin-lattice and spin-spin relaxation time of protons in the human body (T1 and T2 mode, correspondently). To enhance the images definition the contrast agents which accumulated in the diseased area were used. The ways to obtain the contrast agents with high chemical and aggregative stability based on superparamagnetic Fe₃O₄ and biocompatible coating are still under discussion [2].

In this work the original approach to improve the Fe₃O₄ NPs stability by forming the Fe₂O₃ surface layer was presented. Obtained by precipitation method Fe₃O₄ NPs were treated under hydrothermal conditions in the temperature range from 140 to 240° C. XRD, TEM, BET, DLS and VSM methods, Mössbauer and IR spectroscopy were used to establish the optimal conditions of the process. The absorption of dextran and xanthan which used as biocompatible coatings was carried out at 37 and 60° C, respectively. For both types of NPs (Fe₃O₄ and Fe₃O₄@Fe₂O₃) the isotherms at low polysaccharides concentrations are the Langmuir type.

In *in vitro* MRI experiments the obtained nanomaterials (non modified NPs, Fe₃O₄@dextran/xanthan, and Fe₃O₄@Fe₂O₃@dextran/xanthan) demonstrated the negative contrast in both T1 and T2 modes. *In vivo* MRI showed the NPs accumulation in the livers of healthy male mice. So the proposed approach for Fe₃O₄ surface stabilization is an effective and allows to use the obtained nanomaterials for MRI contrast agents.

Authors of this work appreciate Resource Centers of the Research Park of St. Petersburg State University, including Centre for X-ray Diffraction Studies, Magnetic Resonance Research Centre, Centre for Innovative Technologies of Composite Nanomaterials.

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Computations-Aided Design of Novel Drug Delivery Approaches: Tailoring Stability of Covalent Organic Frameworks as Nanocontainers with a Selective Response to Glucose

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One of the key research goals in the modern pharmaceutical industry is the development of new approaches for the targeted and controlled drug delivery. One of the promising strategies towards such smart drugs is their confinement within a nanocontainer matrix that would selectively respond towards the changes in the biological environment characteristic to the conditions specific to a disease resulting in the drug admission to blood. Modern computational chemistry techniques are instrumental to guide the development of new materials to be used as such nanocontainers. Computations can be used to assess how the structural variation in the promising class of materials allows tailoring their properties towards a selective response to the desirable changes in the biological environment.

Herein, we systematically investigated the stability of boron contained covalent organic framework (COF) [1] as perspective targeted drug delivery system of hypoglycemic APIs with a selective response to glucose. COFs are formed via self-condensation of phenylboronic acid yielding polymeric nanoporous materials with B_3O_3 sites as the key structural fragments. Such sites are intrinsically unstable towards hydrolysis and at the same time can potentially be used for the selective binding of cis-diols, e.g. glucose, providing thus with a fundamental possibility to selectively tune their characteristic towards a selective response to carbohydrate. To identify such characteristics, we carried out density functional theory (DFT) calculations on the stability of COFs towards their hydrolysis and selective interaction with the carbohydrate. The computed results suggest that although the full resolution of the COF structure is thermodynamically favorable, the initial reaction with water is an endothermic process. This shows the principle possibility of the kinetic stabilization of the COF structure so that its stability parameters are further optimized by selective modification of the chemical nature of the structure-forming organic moieties of the COF.

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Heat-Conductive Paste

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Modern technology related to heat transfer have the highest requirements to the materials. In this connection we must increase properties and reliability of existing materials, such as heat-conductive pastes. This type of compounds used in military industry, technical and transport industry. Heat-conductive pastes are used in different modern devices for converting thermal energy in electrical energy. Current approaches in this field have some limitations: short range of temperature (-40 from + 300), high toxicity and high electrical conductivity which makes their use limited in many areas of modern industry.

The main purpose of this work – increase the main characteristics of heat-conductive paste retaining dielectric properties.

In our approach we use polydimethylsiloxane as a matrix for paste. To achieve high thermal stability we modify the polydimethylsiloxane by SiO_2 in nanoparticle form obtained by sol-gel principle [1]. Graphitic boron nitride and silicon carbide are used as filler for matrix. These initial powders have suitable properties: high thermal stability, high thermal conductivity and these are dielectrics and they are the most suitable component.

To this day we made experimental pastes compounds for testing thermal stability. These experiments were performed in muffle furnace.

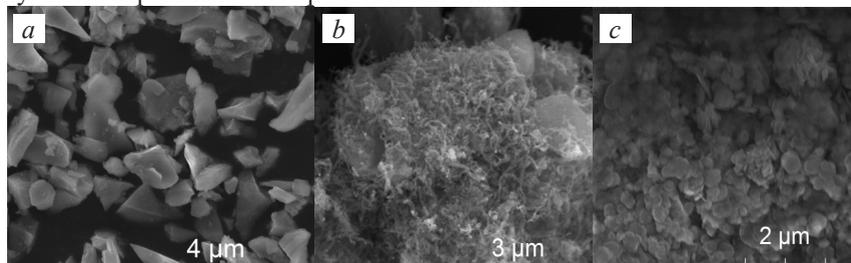


Fig 1. SEM images SiC powder (a), C-nanotubs (b), boron nitride (c).

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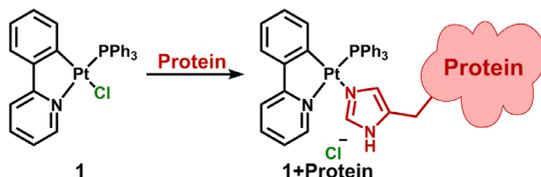
Selective Protein Labeling with Cyclometallated Platinum(II) Complex via Histidine Imidazole Function

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Histidine and histidine-rich proteins can serve as an indicator for a range of diseases: AIDS, asthma, liver cirrhosis and malaria [1]. That's why the problem of searching for the probes which are specific for histidine residues is of particular importance.

Herein we report on selective binding of the platinum complex (**1**) to the histidine and histidine containing proteins, which is accompanied by luminescence switch on. It was found that imidazole ring of histidine reacts with the platinum complex to substitute the chloride ligand by imidazole function.



*Fig. 1. Structure of the complex **1** and its reaction with histidine residue of a protein.*

For better understanding of the interaction of **1** and proteins we thoroughly investigated conjugation of **1** with Ubiquitin (Ubq), which is rather small protein and contains only one histidine residue. ¹⁵N-¹H HSQC NMR spectroscopy and analysis the tripsinolysis products with MALDI mass spectrometry showed that the conjugation of **1** to Ubq occurs via His-68. The results obtained clearly points to a possibility to use **1** for regioselective labeling of histidine-containing proteins.

Acknowledgements. The work was carried out using scientific equipment of the analytical center of nano- and biotechnologies of SPbSPU and the Resource Centers of Research Park of SPSU (Centers for X-ray Diffraction Studies, for Optical and Laser Materials, Chromas Core Facility and Materials Research Centre). Financial support from Russian Science Foundation (16-43-03003).

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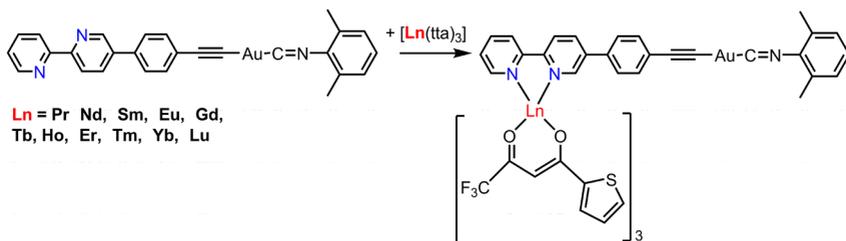
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Mononuclear Au(I) Complexes as Potential Sensitizer for Lanthanide Luminescence

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Unique luminescent characteristics of lanthanide complexes are currently attracting considerable interest. Lanthanide luminescence does not depend on a ligand sphere; each one has its own unique and invariable emission. High emission quantum yield, long lifetime of the excited state, as well as low toxicity, high stability and are capable to TPA, excitation by electric current - all this provides a wide range of application as a light source in OLED technology, bioimaging and ets. Using functionalized luminescent d-metal complexes as ligands provides an opportunity for ligand emission energy to be used as excitation energy for a lanthanide ion. Such an approach is capable of creating a d-f complex with emission in a near IR range when excited by UV light. In this study novel Au(I) complex with free bipyridine function serves as a ligand for various lanthanide cations to form a d-f heterometallic complexes.



Acknowledgements. The authors appreciate financial support from the Russian Science Foundation, grant 16-13-10064. All measurements were performed using the following core facilities at St. Petersburg State University Research Park: Centre for Magnetic Resonance, Centre for Optical and Laser Materials Research, Centre for Chemical Analysis and Materials Research, and X-ray Diffraction Centre.

The Research of the Qualitative Composition and Antioxidant Activity of Yarrow Phenolic Compounds in Conditions of Industrial Pollution

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Under conditions of technogenic environment the changes of biochemical composition and physiological processes of plants take place while the outward appearance is preserved. In extreme conditions the most important mechanism of stability of plants is the activation of biochemical system of antioxidant properties protection, which includes a large number of components exhibiting antioxidant properties, including phenolic compounds. Biological activity of the majority of vegetable polyphenols is caused in many respects by ability to inhibit free-radical processes. Thereof, studying of responses of alive organisms and, in particular plants, on influence of anthropogenous factors and stressful conditions is urgent. The samples of yarrow (*Achillea millefolium*) selected as research objects in this work, are widely used in medicine and are the official medicinal plants of the Pharmacopoeias of different countries. We have the analysis of the qualitative composition and antioxidant activity of phenolic compounds of yarrow growing in the industrial areas of Tver town (Thermal Power Stations, Railcar plant, the Paint and Varnish Factory, The Printing Plant) as a goal. Finished pharmaceutical forms of yarrow of the firm "Health" have been chosen as a control sample. We performed the quality analysis of phenolic compounds in extracts of yarrow growing in Tver's industrial areas using a UV spectroscopy method. For identification of main groups of phenolic compounds as a part of a yarrow electronic spectrum of absorption of water and ethanol extracts of samples in the region of wavelengths of 200-500 nanometers were written down. The antioxidant activity of polyphenols of yarrow ethanol extracts against a stable radical DPPH (1,1-diphenyl-2-picrylhydrazyl) was investigated. It has been established that an amount of phenolic compounds and their antioxidant activity increase in the stressful conditions for yarrow (especially under the influence of the contaminants of TPS-3, the Paint and Varnish Factory). The conducted research allows to draw a conclusion that the extent of stressful influence of adverse factors of the environment, including industrial pollution, on the vegetable organism can be estimated using data of the phenolic compounds content, the main biologically active substances in the plants composition and their antioxidant activity.

Acknowledgements. The authors would like to thank the Eckart Rühl, Professor of the Free University of Berlin for their assistance in the work.

The work was supported by German-Russian Interdisciplinary Science Center (G-RISC).

Oxygen Reduction Catalysts Based on Platinum Nanoparticles Deposited in Transition Metals Polymer Complexes Matrix

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The oxygen electroreduction reaction is the main cathodic process that occurs in the majority of fuel cells. However, this reaction has significant kinetic limitations, and the catalyst is needed for its passing.

The most usable catalysts for this reaction are the metals of platinum group, but their usage is limited due to high price of such materials, which, in its turn, leads to increase in the cost of the energy produced by such type of fuel cell and results in difficulties for successful commercial usage. That is why one of the most important contemporary problems in a field of electrochemical energy sources is lowering of precious metals content in catalysts by fractional, of even full, replacement of them by transition metals oxides. It should be noted that oxides that are to be used in catalysts are subjects to special requirements: they have to be extremely dispersive, have solid connection with the surface of the fuel cell electrode components, and in case of compound catalysts the components must be as evenly mixed as possible.

In this work, the new method of nanodispersed platinum coatings synthesis is suggested: the coatings are modified by copper dioxide and are synthesized from polymeric precursors. Such modification allows to obtain the catalysts the effectivity of which is higher than that nanodispersed platinum. The suggested method is based on template synthesis of platinum particles, in which the polymeric film of copper complex with Schiff base is used as a template. This polymeric layer has a native porous structure, which allows to conduct electrodeposition of platinum in its pores. Further, the polymeric film is removed by the method of basic oxidative hydrolysis, which is accompanied by partial redeposition of copper, in a form of hydroxide, on the surface of platinum particles.

The studies of catalytic activity of the material are conducted on a rotating disk electrode primarily by cyclic voltammetry method. Quartz microcrystal balance and scanning electron microscopy methods were also used.

Acknowledgements. Scientific research were performed at the: Center for Geo-Environmental Research and Modeling (GEOMODEL) of Research park of SPbSU, Interdisciplinary Center for Nanotechnology of Research park of SPbSU, Center for Chemical Analysis and Materials Research of Research park of SPbSU, Thermogravimetric and Calorimetric Methods of Research park of SPbSU.

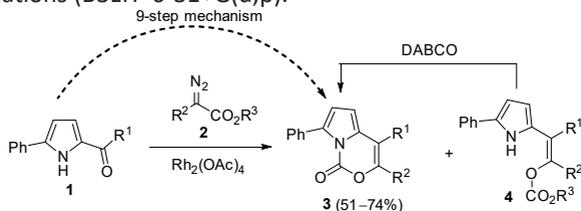
Synthesis of Pyrrolo[1,2-c][1,3]Oxazine Derivatives via Rhodium Carbeneoid Induced Annulation of 2-Aroylpyrroles

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Carbonyl ylides are important reactive intermediates on the way to various three-, five- and six-membered O-heterocycles. One widely used protocol for the generation of carbonyl ylides involves the reaction of rhodium carbenoids with carbonyl function. This method provides good results for the preparation of oxiranes, 1,3-dioxolanes and furan derivatives.

We herein report a one pot procedure for the preparation of novel pyrrolo[1,2-c][1,3]oxazine **3** derivatives from 2-arylpyrroles **1** and diazo carbonyl compounds **2**. This reaction provides a first example of the formation of six-membered N,O-heterocycle by use the diazo compound as annulation agent. This reaction, in general, results in the formation of two main products: pyrrolo[1,2-c][1,3]oxazinones **3** and carbonates **4**. The selectivity of the reaction strongly depends upon the reaction conditions and the structure of the starting compounds. It was found that carbonates **4** cyclize to pyrrolooxazines **3** under the base conditions. A one-pot procedure for the preparation of pyrrolooxazines **3** was developed with the use of 1,4-diazabicyclo[2.2.2]octane (DABCO) on the second stage. The suggested mechanism for the formation of compounds **3** and **4** was confirmed by the results of DFT calculations (B3LYP 6-31+G(d,p)).



Acknowledgements. We gratefully acknowledge the financial support of the Russian Foundation for Basic Research (grant no. 14-03-00187, 14-03-31117) and Saint Petersburg State University (Grant no. 12.38.239.2014, 12.38.217.2015). This research used resources of the resource center ‘Computer Center’, ‘Magnetic Resonance’, ‘Center for Chemical Analysis and Material Research’, ‘Research resource Centre for X-ray Diffraction Studies’ and ‘Chemistry Educational Centre of Research Park’ of Saint Petersburg State University.

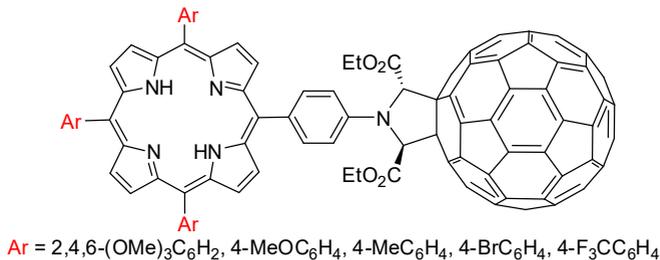
Synthesis of Covalent Porphyrin-Fullerene Dyads with "Face-to-Edge" Orientation of the Chromophores Fixed by *N*-phenylpyrrolidine Linker

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Porphyrin-fullerene dyads are known to be promising materials for photovoltaic and photocatalytic applications [1]. One of the key-properties, defining their practical applicability is the lifetime of the charge-separated state. This parameter depends on many factors, the geometry of the molecule showing the most significant influence on its value. According to literature reports, compounds with "face-to-edge" geometry can form long living charge-separated state, while the lifetime of "face-to-face" molecules is significantly less [2].

The present work is devoted to the development of synthetic route towards donor-acceptor dyads with fixed small separation between face-to-edge arranged chromophores. As a result of this work, the method of synthesis of covalent porphyrin-fullerene dyads connected by *N*-phenylpyrrolidine spacer containing various substituents in porphyrin core has been developed.



The key step of this method consists in 1,3-dipolar cycloaddition of azomethine ylides, generated from porphyrinylaziridines, across C=C bond of fullerene C_{60} . It has been shown, that the proposed method of synthesis of porphyrinylaziridines allows to successfully obtain compounds within wide range of substituents in 5,10,15,20-tetraphenylporphyrin core (from electron acceptors, such as F_3C -, to electron donors, such as MeO-) but gives low yield of product in case of tris(2,4,6-trimethoxyphenyl) substituted substrates, which could be explained by high lability of 2,4,6-trimethoxyphenyl fragment and shows the limits of the method.

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Partial Oxidation of Propylene by Ozone in a gas Phase Reaction

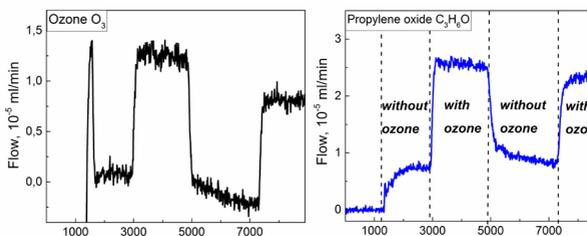
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Propylene oxide (PO) C_3H_6O is an important chemical intermediate for production of various chemical compounds, which have large amount of applications in polyurethane plastics, cosmetics and food industries, etc. Nowadays the worldwide production of PO exceeds 10 million tons per year. There are three main commercialized ways to produce PO: chlorohydrin [1], co-product [2] and hydrogen peroxide [3] way. Despite their high PO selectivity all these methods suffer from several disadvantages such like a lot of co-products, necessity of noble-metal-based catalysts, high concentration of reactants and elevated temperatures. From the other hand direct oxidation of propylene can be promising approach in respect to green chemistry. Therefore the aim of this work was to check the possibility of PO production by direct oxidation of propylene C_3H_6 by ozone O_3 in a gas phase reaction and to make quantitative analysis.

All measurements were carried out in the UHV chamber at room temperature. Ozone was created from O_2 using ozone generator (1% efficiency). Pressures in the experimental chamber during reaction were 10^{-4} , 0.3, 1 and 10 mbar. Ratios between O_2+O_3 and C_3H_6 flows were 2:1, 1:1 and 1:2. Reaction products were detected by quadrupole mass spectrometer. As a result it was found that production of propylene oxide C_3H_6O is possible by direct oxidation of propylene C_3H_6 by ozone O_3 in a gas phase reaction.

Acknowledgements. Author thanks HZB Summer Student Program 2016 for technical and financial support.



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Peculiarities of Critical Phenomena in the System with n-butyl Propionate Synthesis Reaction

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This work deals with considering of thermodynamics and some peculiarities of multicomponent heterogeneous systems with mass-transfer. The development of new physical and chemical approaches to the study of the synthesis processes



Fig. 1. The critical composition of the propionic acid – n-butanol – water system at 303.15 K.

of the ester due to the esterification reaction of propionic acid with n-butanol includes a complex experimental study of chemical equilibrium, solubility, and investigation of critical [1-3]. From the theoretical point of view the aim of the study is the thermodynamic analysis of the transformation of phase diagrams for the quaternary reacting systems with liquid phase splitting. At the same time the practical significance of the delamination problem of reacting mixtures is obvious: such effect changes the technological process of the synthesis. The main object of the study is the system with n-butyl propionate synthesis reaction at 303.15 K. This work presents extremely new data on critical phenomena in propionic acid – n-butanol – n-butyl propionate – water system (Fig. 1).

Acknowledgements. The research is supported by the Russian President's Scholarships (SP-2140.2016.1).

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Novel Liquid Electrolytes with High Ionic Conductivity

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With the progress of modern society, the role of electric energy in our life has increased, and thus energy storage devices are drawing more and more attention.

Polyoxometalates (POMs) are multifunctional materials, which have an extensive use in catalysis, medical industry, biology, and materials science[1], due to the unique combination of their physical and chemical properties, including high stability of oxidized and reduced forms, and the possibility of repetitive electron transfer. These properties give grounds for believing that POMs can be very suitable for the role of electrolytes in energy storage devices[2].

The paper presents inorganic ionic liquids with the following composition: $\text{Li}_{13}[\text{Ln}(\text{TiW}_{11}\text{O}_{39})_2] \cdot x\text{H}_2\text{O}$, where Ln is lanthanide.

The scope of the study: the technology of synthesizing POM of the said composition was improved, the change of materials' properties depending on the included components was analyzed, and the most stable samples, which have the best conductivity characteristics, were educed.

The properties of structural composition were studied through X-ray fluorescence analysis, thermogravimetric analysis and mass spectrometry with electrospray ionization. The examination of electrochemical properties of synthesized materials was conducted through the methods of cyclic voltammetry.

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Critical Phenomena for the Quaternary System Acetic Acid – Ethanol – Ethyl Acetate – Water at 333.15 K

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The systems that have both of chemical and phase transformations are widely applied in organic synthesis of esters as solvents. But the critical phenomena observed in these systems are poorly investigated, despite the significant impact on the development of thermodynamics.

The object investigated is heterogeneous system with ester synthesis reaction acetic acid - ethanol - ethyl acetate - water. The solubility and critical phenomena were studied in a number of ternary and quaternary systems by the “cloud point technique” method. The results are presented in concentration tetrahedron where red curve is the critical curve (Fig. 1). Some results for these systems, obtained at temperatures of 293.15, 303.15, 313.15 K, were presented in [1, 2] accordingly. These results about the critical states were compared with ones obtained at 333.15 K in concentration tetrahedron of compounds. Some regularities have been established.

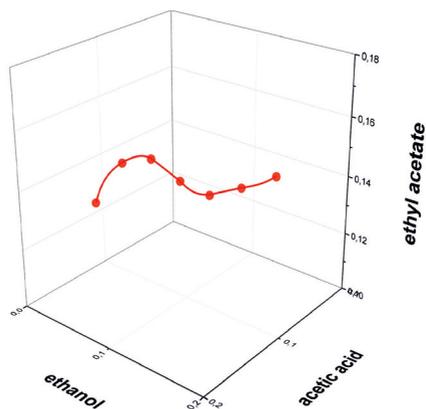


Fig. 1. The critical curve in acetic acid-ethanol-ethyl acetate-water system at 333.15 K.

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Synthesis of Fe₃O₄@Cu Nanoparticles and their Functional Properties

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Magnetite (Fe₃O₄) nanoparticles (NPs) attract great interest because of their magnetic, electric, and adsorption properties [1]. It can be synthesized by the precipitation method in inert atmosphere to prevent surface oxidation of Fe₃O₄. The copper NPs are applied as an antibacterial material in medicine and biotechnology [2]; also they are used in conductive ink, membranes and microchips [3]. They are often produced in the polyol media by reducing of copper ions.

Last time the synthesis of the core-shell NPs is widely discussed because it gives an opportunity to make a new material with special and unique properties. In addition, it helps to protect the «core»-substance from oxidation and aggregation [4]. Therefore, the purpose of this project is synthesis and functional properties investigation of Fe₃O₄@Cu nanoparticles.

The structure of obtained NPs was confirmed by complex of independent methods (XRD, TEM, BET). The resistance vs temperature dependence was study by impedance spectroscopy. It was found that nanoparticles demonstrated the semiconductor behavior and the resistance and activation energy values decreased with increasing of Cu amount. The impact of the shell size on NPs magnetic properties and the weakening of the interaction between NPs were shown by VSM method. It was also detected that the NPs exhibit significant antibacterial activity against gram-positive bacteria *Micrococcus*.

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Thermal Decomposition of Gaseous Borazine: Diffusion-Controlled Reaction on the Surface

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Thermal decomposition of gaseous borazine was studied. Borazine $B_3N_3H_6$ was prepared by standard procedure [1] and purified by distillation in vacuum. Saturated and unsaturated vapor pressure of borazine in the temperature range $-196\text{ }^\circ\text{C} - +200\text{ }^\circ\text{C}$ was measured by static tensimetric method with membrane null-manometer [2]. Three series of measurements, consisting of fast freezing with liquid nitrogen, heating and long thermostating of borazine at $100\text{ }^\circ\text{C}$ and at $200\text{ }^\circ\text{C}$, have been performed. Besides borazine, hydrogen and small amounts of at least two unidentified compounds (supposedly ammonia and polyborazines) were observed in gas phase. Assuming that borazine does not decompose at low temperatures, partial pressures of the components were calculated. The ratio of the amount of evolved hydrogen to the amount of decomposed borazine is 1.8 ± 0.1 , suggesting formation of $[H_{1.2}B_3N_3H_{1.2}]_n$ polymer, in agreement with earlier observations [3, 4].

Decomposition reaction rate at 373 K and 473 K is almost the same, indicating that reaction is diffusion-controlled. Obtained results show that decomposition of gaseous borazine occurs only on the surface of the glass apparatus and activation energy for the rate-limiting chemical step is small. Small energy barrier is in agreement with experimentally observed decomposition of liquid borazine at room temperature.

Acknowledgements. Financial support of SPbSU (project № 12.38.255.2014) is gratefully acknowledged.

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Synthesis and Photophysical Properties of a New Dinuclear Platinum(II) Complex That Features Unusual Low-Energy Emission

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Currently, a large number of phosphorescent transition metal complexes have been synthesized and investigated. In this respect, platinum(II) complexes are of particular interest, as these species possess high luminescence quantum yields, good stability and are relatively simple to prepare. Such properties make their application prospective in different areas of modern technologies related to the use of luminescent compounds. One such area is bioimaging, where compounds that emit in the near infrared region (NIR) of the visible spectrum (the so-called transparency window of biological tissue), are uniquely superior compared to other emitters. At the moment, only few such emitters based on transition metal complexes are known.

We previously prepared dinuclear platinum(II) complexes 1–3 (Fig. 1), the emission of which lies in the orange-red part of the spectrum. In order to shift the emission bands to the NIR region an analogous cyclometalating ligand was synthesized, the phenyl substituents of which are replaced with thienyl groups. Based on this ligand, complex 4 was obtained (Fig. 1). The structure of this complex was established by means of a number of physico-chemical analytical methods, and a detailed description of its photophysical properties will be given in the stand report. The luminescence of complex 4 features two emission bands with maxima at 692 nm and 754 nm, and 75% per cent of the spectrum lies in the NIR part, which makes this compound and its water-soluble derivatives suitable for in vivo bioimaging.

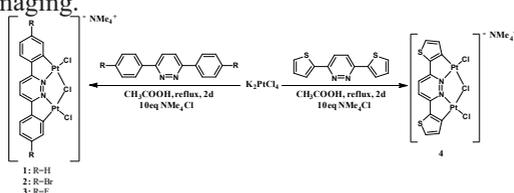


Fig. 1. Synthesis of complexes 1–4.

Acknowledgements. The authors appreciate financial support from RSF grant № 16-43-03003. The equipment of the following core facilities at St. Petersburg State University Research Park was used: Centre for Magnetic Resonance, Centre for Optical and Laser Materials Research, and Centre for Chemical Analysis and Materials Research.

Arc Atomic Emission Spectral Analysis of Viscous Organic Liquids

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Viscous organic liquids are widespread in various industrial sectors. Technical properties of these objects depend on microelement composition. For example, the strength of adhesive joints depends on the amount of metal-based fillers in glue. Presence of heavy metals in medical adhesives is unacceptable. From an environmental point of view, it is important to avoid the release of toxic elements from coagulants and flocculants for wastewater treatment. Thus, it is important to determine the metal content in liquid organic fluids.

Because of macro components of complex organic matrix makes it impossible to analyze these samples directly: most of mass and optical spectral methods require preliminary sample preparation. The stage has many disadvantages: it is a labor-intensive process, takes a long time, requires a wide range of chemicals, can lead to random and systematic errors. That is why the development of techniques that simplify the analysis is an actual problem in modern analytical chemistry.

It is known, that atomic emission analysis in AC arc with spectrum excitation of dried residue allows the determination of metals in biological fluids. However, objects under this study have much higher concentration of organic components compared with biofluids. The aim of the work is to find possibility of using mentioned method in analysis of objects with complex organic matrix. Different ways of simplified sample preparation are investigated in the study to reduce matrix influence. Accuracy test was made by reference methods. Reports contain metrological characteristics of developed technique as well as examples of analysis of real samples.

Acknowledgements. Part of the research was done using the equipment of the Educational Resource Center of Chemistry of Research Park of St. Petersburg State University.

B.Geo- and Astrophysics

The Analysis of Temporal Variations and Distributions of Cloud Liquid Water Path Based on Satellite and Ground-Based Measurements near Peterhof

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Cloud Liquid Water Path (CLWP) is a measure of the total liquid water contained in a cloud in a vertical column of atmosphere except snow, ice, e.g. This parameter is an interesting area of research. It links the hydrological and radiative components of the climate system. Cloud water has a significant influence on radiative transfer because of its functioning as warming or a cooling factor as it can reflect solar energy back into space. That is why cloud water can provide either positive or negative feedbacks on climate changes [1].

CLWP data are difficult to retrieve due to inhomogeneity in space and time.

Microwave radiometers (MWR) are widely used for CLWP measurements. There are two main types of MWRs depending on the type of carrier: ground-based MWR and satellite MWR. First type is represented by RPG HATPRO. It has high spatial and high temporal resolution (one measurement per 2 seconds) [2]. Second type, represented by AMSR2 on board of the satellite GCOM-W1, on the contrary, has low spatial (pixel with more than 10 km from each side) and low temporal (once a day) resolution [1].

The analysis of the data retrieved both from RPG HATPRO and AMSR2 is focused on:

- Investigation of temporal variation and distribution of both retrievals (RPG HATPRO – hour mean LWP, Peterhof (59.88107°N, 29.82597°E); AMSR2 – LWP, Ladoga Lake(61,375 N, 31,125 E); Baltic Sea(58,6250 N, 20,3750 E))
- Comparing the data retrieved from both MWRs.

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The Investigation of the Space Distribution of Magnetic Stars

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Magnetic stars are made up of main sequence stars with O, B, A, F spectral types, showing the large-scale magnetic fields with strength between the few hundreds and tens of thousands Gauss. These stars magnetic field origin is not totally clear. It was believed that it appears due to dynamo action, like the solar magnetic field formation [1]. At the same time, it should be kept in mind, that the Sun has no regular, strong large-scale magnetic field and it isn't a magnetic star. In early type stars the dynamo action is counterproductive and it wants some kind of seed-value field [4].

The hypothesis, that the star magnetic field is the fossil remnant of the field of a large molecular cloud whereof the star has been formed is popular now [2]. So, one can predict the increase of the magnetic stars number in the regions with a strong galactic magnetic field: in spiral branches, star-forming regions, etc.

At present, catalog [3] is the most complete. It consists of stars, whose fields had ever been measured before 2009. According to the definition we have divided the catalog into three parts: stars with the rms magnetic field strength $B > 100$ G was accepted as “suspected to be magnetic”. Some of the “suspected to be magnetic” stars satisfying both conditions $\langle Be \rangle > 2\sigma$ and $\chi^2 > 1$ are considered to be magnetic.

The galactic coordinates and other parameters of all O, B, A, and F type stars were taken from SIMBAD. We have investigated the catalog stars distributions throughout the galactic coordinates and the distance together with all stars distribution. We have detected the stars density enhancement in the Orion Nebula direction. At the same time this density is low in the solar neighborhood. Basing on these facts we can conclude that the “fossil field” hypothesis seems to be preferable.

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Implementation of the IRI Model into the Software for HF Radio-Paths Simulation

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The study of high frequency (HF) radiowave propagation in the ionosphere is of great interest nowadays. This is due not only to the development of science, but also to a great practical applicability of this field of knowledge. There are many programs for simulation of HF radiowave propagation. The program which is used to simulate vertical sounding of the three-dimensional inhomogeneous ionosphere by electromagnetic waves of HF range requires the background ionosphere, which can be built with the help of the data obtained from the vertical ionospheric sounding stations. However, there are some times when these data are absent for various reasons. In these cases it is possible to substitute the data obtained from ionosondes with the data taken from ionospheric models.

The paper is devoted to the usage of the data obtained on the basis of ionospheric IRI model for the HF radio-paths simulation with the help of known software. The necessary IRI model database, which is used to build the background ionosphere, is created. Then the simulated ionograms and the experimental data of the ionosondes are compared. It was found that sometimes the IRI model does not correspond to the experiment. When the model gives not very good results, adaptation of the IRI model to the real parameters of the ionosphere is produced. The usage of IRI model for the HF radio-path simulation may be useful when (i) it is not possible to use the ionosondes and when (ii) it is needed to make a prognosis for the next day.

Application of Seismoacoustic Profiling for Study Geological Structure of the Upper Part of Lake Ladoga Section

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There are considerable debate about formation and history of the development of Lake Ladoga.

Research expedition organized by the Institute of Earth Sciences, St. Petersburg State University, the Center of seismic data analysis Moscow State University and the Institute of Water Problems, Karelian branch of RAS was carried out in 2015 in the southern part of Lake Ladoga. The expedition was aimed to detailed study of geological structure of the upper part of Lake Ladoga section. Obtained data clarified the characteristic of geological structure:

- The real borders of earth formations were traced;
- The power of Quaternary sediments was appreciated;
- The outputs Riphean rocks were identified further south than it was previously thought;
- New data related to the nature of the lake bottom relief was obtained.

The geophysical investigation by seismoacoustic profiling in the Lake Ladoga showed high quality, reliability, efficiency and accuracy of the research findings. A combination of single-channel and multi-channel observation systems, boomer and sparker sources allowed to explore Lake Ladoga section at a sufficiently great depth with high resolution. This fact once again confirms the advantages of the seismoacoustic profiling for study of the upper part of the section in the shallow waters.

Nocturnal Emission of CO₂ and CH₄ in Boundary Layer at the Peterhof Station for 2014 and 2015

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Carbon dioxide and methane are the major long-lived greenhouse gases in the Earth atmosphere, which concentrations have increased significantly since the preindustrial period. Satellite, aircraft and ground-based observational systems are involved into the investigations of spatio-temporal variations of CO₂ and CH₄ in the atmosphere. However, the most practical way to monitor air quality is keep track of magnitude of emission for different countries. This is why continuous monitoring of CO₂ and CH₄ concentrations in the ambient air is being carried out at the Peterhof site since 2013. It gives us an opportunity to estimate emission intensity of CO₂ and CH₄ for a suburban territory of greater St. Petersburg using the events of the nocturnal accumulation of contaminations in the atmospheric boundary layer. We obtained that the average emission intensities for CO₂ and CH₄ estimated for 2014-2015 are of 5335 ton/km² year and 38 ton/km² year, respectively.

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Properties of Inhomogeneous Viscous Waves

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This research looks at viscous waves with a complex wave vector. Such waves are considered transverse and inhomogeneous [1]. The study offers numerical analysis of phase velocities and velocities of equal amplitudes of oscillating speed of liquid particles in a viscous wave, which is excited by a harmonically oscillating plane. It is shown, that phase velocities vary for different phases. So the phase speed is $c_{ph} = 0.84 \text{ m/s}$ for the phase $\varphi = \pi$ rad, when oscillating speed reaches its maximum. It is close to the theoretical calculations offered in [1]. When the oscillating speed is minimal and the phase equals $\varphi = \pi/2$ rad, then the phase speed is $c_{ph} = 0.68 \text{ m/s}$. The error of defining the phase speed is 14 %.

Surfaces of equal amplitudes are curvilinear (Fig. 1). They become planes in certain moments of a period T of particle oscillation. If the wave is represented as $v=v_0 e^{-x/\delta} \cos(\omega t-k_0 x)$, where δ is boundary layer thickness, then the moments are the ones when oscillating speed is $v=0 \text{ m/s}$ and acceleration reaches its maximum. These are $t = T/4, 3T/4$. It testifies that oscillating velocity and the wave vector \mathbf{k} change their relative positions in time. It can be noticed from the Fig. 2, if we track the time displacement of the points of oscillating speed minimum for each curve. The results circumstantially validate the ones in [2, 3].

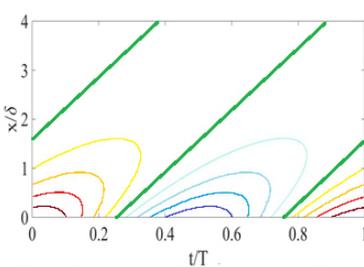


Fig. 1. Contour lines of liquid particles oscillating speed in an inhomogeneous wave

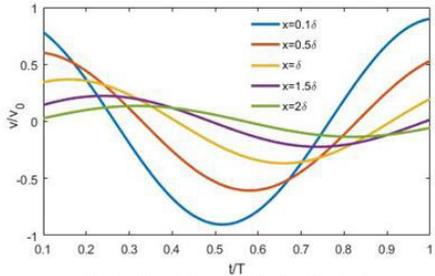


Fig. 2. Visualizing of oscillating for different distances from the oscillating plane

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The Study of Cloud Condensation Nuclei Properties of Background and Anthropogenic Aerosol Particles for Season 2014

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Atmospheric aerosols are known to have a direct effect on climate through scattering and absorbing incoming solar radiation. They also indirectly affect climate by acting as cloud condensation nuclei (CCN) and modifying cloud forcing and hydrological cycle [1]. Aerosol particles acting as CCN cause changes in droplet number affecting albedo and persistence of clouds. Thereby they control the microphysical properties of cloud systems under appropriate atmospheric conditions. The determination of this ability of aerosols is one of the key objectives of aerosol climatology [2].

The researches of CCN properties allow to find a connection between the sources of aerosol particles and condensation activity that depends on their size, chemical composition and hygroscopicity. The influence of chemical composition can be described using the effective hygroscopicity parameter κ [1]. At the present time for such studies special spectrometers of CCN, which allow to carry out investigations of different climatic zones, are widely used.

In this study the measurement data on two stations, near big megapolis with high level of anthropogenic pollution and in the Siberian region with background values, where the main contribution comes from biogenic emissions of natural sources, are represented for spring and summer season 2014. Average value of hygroscopicity parameter κ were 0.34 ± 0.19 and 0.27 ± 0.13 , respectively.

Acknowledgements. This work was supported by the Geo Environmental Research Center “Geomodel” of the Saint-Petersburg State University.

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Own Rotation of Single Dust Particle in Complex Plasma

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Interest of single dust particle own rotation in dusty plasma is caused by it's close connection with the process of charging of dusty particle by surrounding plasma flowing on it's surface. Because of this, it is possible to measure the charge of dusty particle by contactless optical methods. Also, charged rotating particle has the value of magnetic moment up to 10^5 . Bohr magnetons so in the external magnetic field can be observed effect of alignment magnetic moments according to magnetic induction. Thus, explanation of mechanisms of single dust particle own rotation leads to a better understanding of interaction of complex plasma with the external magnetic field and to understanding of some collective processes, such as self-organisation of dusty crystals.

There are two known mechanisms that can generate rotation of dust particles: azimuthally asymmetrical flow of plasma on the surface of dusty particle and symmetrical flow on the asymmetrical particle.

Other factors, such as the inclusion of external magnetic field only can effect on already generated rotational motion.

In the present work the influence of the plasma flow through the local area (Debye sphere) and the influence of the whole discharge current on the single particles own rotation were studied.

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Impact of Solar Proton Events on Dynamics of Chemical Composition of the Polar Atmosphere

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This paper presents a study of changes of chemical composition of the polar atmosphere, namely hydroxyl hydrogen OH via changes of atmospheric ionization, and their impact on the vertical profiles of different elements including into HO_x. Changing of ionization rate is due to the external flux of protons generated by solar proton events and/or by variability of galactic cosmic rays. Several solar proton events (SPE) that occurred in January 2005 caused the increase of the ionization rate at the polar atmosphere by several orders of magnitude. Also, during to these SPE occurred two Forbush decreases. The decreases of intensity of galactic cosmic rays lead to reduction of ionization rates at the middle atmosphere. The results of present research are presented in the form of spatial-temporal distributions of OH before and after the SPE in January 2005. In this study, we confirmed that increase in the rates of ionization leads to significant fluctuations of OH in the upper stratosphere and mesosphere. At the first time we have revealed that the reduction in ionization, caused by Forbush decreases, leads to a significant reduction of OH in the lower and middle stratosphere. All changes lead to variability in the profiles of HO_x in the polar night atmosphere.

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Analysis of Local and Remote Measurements of Ozone

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Surface ozone is a secondary atmosphere pollutant and it can be used as a benchmark of general air pollution. Usually, due to the transition mechanism, the ozone concentration in a suburban area is larger than inside the city. At the Peterhof SPbSU measurement station, the regular measurements are performed since 2013 using automatic photometric gas analyzer “49iOzoneAnalyzer”. The surface concentration data is compared with the results of troposphere ozone measurements, which have been performed using Fourier spectrometer IFSBruker 125HR, and with the data of Zelenogorsk, Sestroretsk, and Kronstadt stations. Besides that, the connection between the variations of surface ozone and NO_x concentrations at the Peterhof station is analyzed. It is shown that, in most cases, daily average values of ozone concentration at the Peterhof station exceed the Russian air quality standards (30 µg/m³). The maximal ozone concentration values during the daily variation are reached at day time, during the annual variation they are reached in spring. At other stations, the same dependence is observed. In winter time, the negative correlations with the troposphere ozone are often observed. In spring-summer time, as usual, the correlations are positive. Comparison of O₃ and NO_x concentrations demonstrates negative correlation during the whole measurement period.

Assess of Pit Slope Stability in Case of Changes of Mechanical Properties of Rocks due to Field Development in Permafrost

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Open pit mining process due to its effectiveness becomes more and more widespread. Research of pit slope stability is necessary for providing safe and efficient mining and can help to preserve economic and ecological damage in case of crushing the pit slope.

Volkovskaya ore zone of Severnoe field is a study area of our work and it is situated in Magadan region, where one of the main factors which have a negative effect for mining is permafrost. Due to human activity on this area temperature of permafrost has a tendency to increase and therefore their mechanical properties may change (specific gravity, moisture, porosity). Moreover, frozen soils are quite firm as water is the cement, but when thawed they are saturated by the liquid water. Therefore in thawed condition massive of rocks has a piezometric level, so in this case hydrostatic weighing also reduce stability of whole massive. As a result it reduces their strength, waterproof and anticripping properties. In this case difficulties with determination the optimal angles for pit slope occur. Main factors occurring change in permafrost are removal and blackening of the snow coverage and removal plant coverage.

According to plan where will be the quarry with several benches with different angles of developing, which vary from 25° to 70° . Using Slide 6.0 software factor of safety was defined for each slope in frozen and thawed condition. Janbu's and Bishop's method were used for making calculations. According to measuring data investigated in these two cases rocks are identical, but when thawed they have lower cohesion and angle of internal friction.

According to results, for all elements when frozen factor of safety more than acceptable, therefore they are in the stable state. But massive of rocks will be unstable at summer when thawed if angle of pit slope more than 30° . It means that during field development adverse geological processes may occur. The main reason for it is changes of mechanical properties due to anthropogenic factor and inappropriate slope design [1].

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Kinematic Calibration of Distance Scales for Planetary Nebulae

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Planetary nebulae remain a class of objects with a very big uncertainty of their heliocentric distances. Despite numerous attempts on solving the problem, which definitely interferes planetary nebulae studies, there isn't still a consolidated point of view.

One of the reasons behind it is a number of different astrophysical approaches, relating upon even more of external assumptions, resulting in identical data being treated differently. A possible solution is usage of another method, preferably not based on astrophysical models and independent of external assumptions, for validating and calibrating the existing distance scales, revealing the flawed and fine ones.

Such a method, first developed for estimation of distance for the center of Milky Way, was reworked and remastered to serve the new goal for the uneasy sample of planetary nebulae of the galactic disc. Several improvements were added, focusing on purging the sample of non-disk and other misclassified objects. In general, the implemented algorithm handles the task of determination of parameters of galactic kinematics and of the algorithm itself on its own.

The algorithm described above was applied to several modern planetary nebulae distance scales, pointing out their strong and weak points, allowing us to select the best ones.

fluence of a Starting Model on the Travel-Time Tomography Solution

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The first step in solving any of travel-time tomography problems is linearization: a starting model is chosen, travel time residuals relative the model are calculated, and finally the problem is reduced to linear system of equations that relates the travel time residuals and parameters of the velocity correction relatively to the starting model. We show that such approach for solving the tomography problem leads to the solutions that depend on the choice of the starting model.

We consider the tomography problem that uses travel times of diving waves when sources and receivers are located on a horizontal surface. In such a case the starting model is chosen as a function of only vertical coordinate $V_0(z)$ and the tomography problem is reduced to a search of the velocity corrections at different depths that depend on horizontal coordinates. The starting model should be chosen in a simple form (linear or piecewise linear function) in order to calculate travel times and the wave paths (rays) easily. The vertical section is divided by horizontal layers and horizontal velocity corrections are estimated in each layer. So the problem is formulated as a search of the corrections $\delta V_k(x,y)$ in each k-th layer, and the final solution is represented as $V(x,y,z) = V_0(z) + \delta V_k(x,y)$ where $z_k < z < z_{k+1}$. However it was found that such a solution depends on the starting model because the tomography solution depends on configuration of the rays and in turn on the starting model. This can be easily understood if the velocity corrections are assumed as constant values in cells: in different starting models the rays may cross different cells, so that the data (residuals) contain information about the velocity corrections in different cells.

More appropriate method for solving such a problem was earlier proposed (Yanovskaya, 2012). The velocity corrections are assumed to satisfy a smoothness criterion analogous to that used in surface wave tomography. By numerical modeling we show that even similar velocity profiles $V_0(z)$ result in different solutions $V(x,y,z)$ if the gradients of $V_0(z)$ are different. An approach for a proper choice of the starting model is suggested.

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Photometric Interpretation of Blazar AO 0235+164 Behaviour

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Among the great number of controversial issues the most topical one both for theoretical and observational astrophysics presently is a problem of active galactic nuclei investigation. To explain the behaviour of blazar AO 0235+164, which has been being observed at the LX-200 telescope (SPbSU) since 2002, the method of analyzing developed by V.A. Hagen-Thorn and S.G. Marchenko [1] was used. It is based on the assumption that in case of observational data lying on the straight line in the absolute Stokes parameters space $\{I, Q, U\}$ (for polarimetry) and the fluxes space $\{F_1, \dots, F_n\}$ (for photometry) relative Stokes parameters and relative flux ratios stay unchanging, and, consequently, the only one source is corresponding for the variability of general value of flux.

In given paper, the photometric interpretation of blazar behaviour is presented. Furthermore, the flux and flux-flux diagrams are obtained for 3 periods of object monitoring: 2006-2007 and 2009 (outbursts) and 2009-2014 (decline). Eventually, according to diagrams analysis the supposition of the single source correspondence was done.

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Spectra Analysis of Galaxies with Known Super Massive Black Hole Masses

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Coevolution of super massive black holes (SMBHs) with their host galaxies proposes the interesting problem of galaxy evolution and active galaxy nuclei (AGN) feedback [1]. Previously, the relations between SMBH masses and kinematic properties were analyzed by Zasov et al [2]. In future investigations correlations of SMBH masses with stellar population properties will be added.

The series of long-slit spectra of disk galaxies with known black hole masses were obtained at the 6-m Russian telescope of the Special Astrophysical Observatory. The post processing program AGAFIA (Adaptive GALaxy spectrum Fitting and Analysis) was developed to derive both kinematical characteristics and properties of the stellar population using an adaptive binning procedure and ULYSS software package.

The example of AGAFIA output for NGC 5548 is presented in Fig. 1.

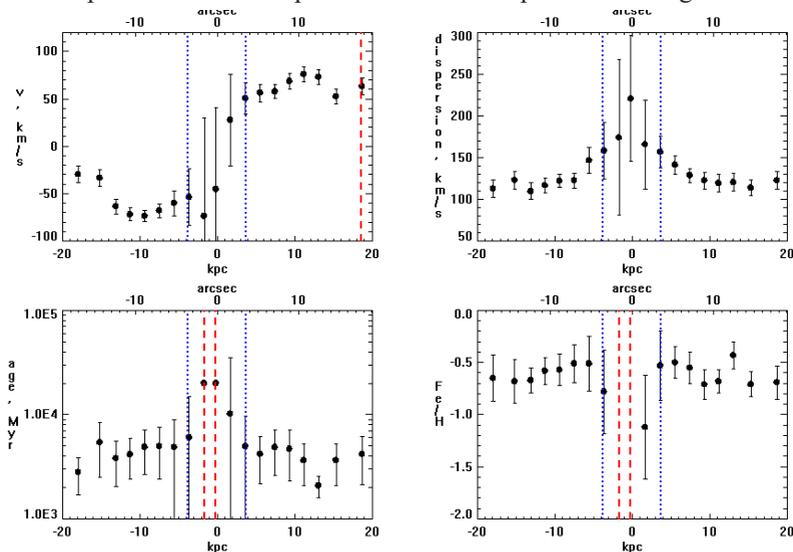


Fig. 1. Radial velocity, dispersion, age and metallicity profiles for NGC 5548.

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Interstellar Medium and HII Bubbles in Dwarf Galaxies: Observations

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The laws of interactions between interstellar medium and stars, also known as stellar feedback, are still on scientific discussion. Dwarf galaxies with solid-state rotation are great for observing and modeling feedback effects. We present deep H α photometry and panoramic spectroscopy of few dwarf galaxies made by 6-m Russian telescope (BTA) with SCORPIO-2.

Star-forming regions are surrounded by expanding HII shells, so-called “bubbles”, blown by stellar wind provided by young blue (OB) stars [1, 2]. Their expansion velocity is an independent way to estimate age of star-forming region. We discuss classical methods for determination their expansion velocities and offer a new one.

We describe groups of star-forming regions that can be described as star-forming complexes because of their morphology, HI background and surrounding stellar population. Also note that star-forming complexes, located on the rim of kpc-scale HI supergiant shell, have close ages. We provide observational evidence of positive feedback from young stellar population that can trigger star formation in surrounding regions, forming supergiant shells.

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Velocity Determination of Seismic Waves by Genetic Algorithm

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A Genetic algorithm (GA) is an optimization technique that arrives at a solution using a method that simulates the process of evolution in biological systems. GA are very important methods for the solution of non-linear problems. The basic steps in GA are: coding, selection, crossover, mutation and choice.

In the previous article we used the GA for the estimation of the velocity for the gradient layer. The synthetic seismogram was calculated by the finite-difference method. The obtained results showed higher effectiveness GA for the velocity estimation. In this paper we have complicated model. Now the velocity varies not only with depth but also on the surface.

Comparative Properties Prominences in the 16th Cycle of Activity

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Completed digitization of daily sketches solar prominences on observational data for the period 1922-1934 years. Prominences observations were made of the international network of visual observation of solar spectroscopy, which included Roman Observatory, Arcetri, Catania (Italy), Kalocsa (Hungary), Madrid (Spain), Medon (France), Zo-se (China), Odessa (Russia), Zurigo (Switzerland). The first regular observations relate to 1869 and have been launched A. Secchi and P. Tacchini published in 1872 in the writings of “Memorie Societa Degli Spectroscopisti Italliani”, and later in 1922 in the writings of “Transactions of the International Astronomical Union”

These are detailed drawings of structures of prominences, presented in the form of a sweep limb and objects above it for each day. For digitization prominences was developed software to allocate and memorization shape of prominence, as well as their origin. Total for the period 1922-1934 years was allocated over 55 thousand prominences, which allows us to study their properties at the different latitudes. This proceedings presents an analysis of the distribution area, the height positions of prominence in the 16th cycle of activity, as well as a comparative analysis of the properties of prominence with later observations on the Kislovodsk Mountain Astronomical Observatory GAO RAN during the period 1957-2016.

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Analysis of Abnormal Aerosol Optical Depth near Saint-Petersburg in February 2014

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Changes of atmospheric aerosol and gaseous compounds are the most important factors influencing atmospheric radiation and, therefore, affecting the whole climate system. The knowledge of long-term variations of aerosol optical thickness can significantly affect the assessment of climate change.

In SPSU (Peterhof) the continuous measurements of aerosol optical and microphysical characteristics have been performing since 2013 using automatic sun photometer Cimel CE 318, standard sounding instrument of the Aerosol Robotic Network (AERONET), global aerosol monitoring system.

Analysis of temporal dependence of retrieved aerosol optical depth (AOD) for 2014 assigned an abnormal peak value the 27 and 28 February.

Comparison with others stations of aerosol network and plotting of backward trajectories of air mass movement using HYSPLIT model were carried out for explication of mentioned atmospheric phenomenon.

C. Mathematics and Mechanics

Badly Approximable Numbers and the Growth Rate of the Inclusion Length of an almost Periodic Function

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A continuous function $f: \mathbb{R} \rightarrow \mathbb{C}$ is called almost periodic if for every $\varepsilon > 0$ the set

$$\Omega_\varepsilon(f) = \{\omega \in \mathbb{R} \mid \sup_{t \in \mathbb{R}} |f(t + \omega) - f(t)| < \varepsilon\}$$

is relative dense, i.e. there exists $L(\varepsilon) > 0$ such that the set $[a, a + L(\varepsilon)] \cap \Omega_\varepsilon(f)$ is not empty for each $a \in \mathbb{R}$. The number $L(\varepsilon)$ is called an inclusion length. If

$$f(t) = \sum_{j=1}^n A_j e^{i\lambda_j t},$$

where $A_j \in \mathbb{C}, \lambda_j \in \mathbb{R}$ and all the exponents λ_j are rationally independent, we prove that

$$L(\varepsilon) \geq \left(\frac{1}{\varepsilon}\right)^{n-1+o(1)} \quad \text{at } \varepsilon \rightarrow 0$$

Here we use methods from dimension theory [1]. From a result of K. Naito [2-3] it follows that this lower asymptotic bound is reached for the case of simultaneously badly approximable exponents. K. Naito used the upper estimate of $L(\varepsilon)$ to estimate the fractal dimension of almost periodic attractors. So, our result can be useful not only to understand the nature of simultaneously badly approximable numbers and almost periods, but also for more detailed understanding of the structure of almost periodic attractors.

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The Use of Differential Inclusions in the Investigation of an Elasto-Plastic Oscillator

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The elasto–plasticity theory describes the behavior of bodies that present an elastic reponse before a certain limit, called yield surface, is reached [1]. After this, the body presents a plastic response which is usually irreversible. The hardening effect represents the modification of the yield surface due to plastic deformations. In this paper, a simple elasto-plastic model is described [2].

The given dynamical system is studied as a differential inclusion. The monotone operator theory is applied to prove the existence of the solution [3]. Another way to obtain this result is described using the definition of the classical solution of differential inclusion and introducing the Lipschitz condition for multivalued functions [4].

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Nonlocal Analysis of Equation with State-Dependent Delay

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Theory of state-dependent delay differential equations is becoming more important for applications today. In this work we consider logistic equation with state-dependent delay:

$$\dot{N} = \lambda N [1 - N(t - T(N))] . \quad (1)$$

Let $T(N) = 1/2 + 1/(1 + N(T))$. We assume λ is sufficiently large, so equation (1) is singularly-perturbed. The main problem is to investigate its nonlocal dynamics. Its local dynamical properties were researched in [1].

Particularly in this work we investigate existence of nonlocal periodic solutions of equation (1). There is the method of the big parameter [2], which allows to research existence of nonlocal relax periodic solution of singularly-perturbed equation with delay. The essence of this asymptotic method is to construct Poincare map of a subset of solution's set and to prove it has a stable fixed point. The technique of step-by-step integration of delay differential equation makes such constructions possible.

With the help of this method we proved the existence of nonlocal relax periodic solution of equation (1), and also obtained asymptotic approximations for its most important characteristics, such as the first maximum point $(t_M(\lambda))$ and maximum value $(N(t_M(\lambda), \lambda))$.

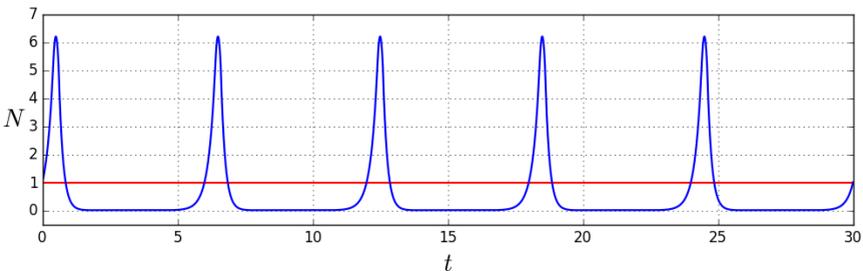


Fig. 1. Solution of (1) with i.c. $\exp((\lambda+1/2)t)$ under $\lambda=23\pi/20$.

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Steady-State Crack Propagation in a Brittle Periodic Structure under a Moving Load

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The development of cellular materials led to the wide range of their mechanical properties which sometimes are superior to those of conventional materials. The analysis of dynamic fracture propagation in such materials remains to be significant in the modeling the performance of such materials. Successful approach to study such problems was proposed by Slepyan [1] and further developed by him and his colleagues [2, 3].

We use this method to consider the crack propagation in the structure shown in Fig. 1 (mode III fracture). We assume that steady-state crack growth, i.e. when crack moves with constant speed v , is a result of application of force which location can move with constant speed v_f .

We obtain a solution of the problem utilizing Wiener-Hopf technique, derive the dependence between crack speed and loading parameters and discuss physical meaning of the derived solution.

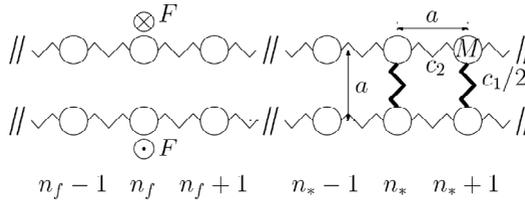


Fig. 1. Double chain of oscillators of equal masses M with linear springs of stiffness $c_1/2$ (fat lines) between chains, springs with constants c_2 along the chains (normal lines), a – equilibrium distance between oscillators, n_ represents the crack tip, n_f – location of applied load of magnitude F .*

Acknowledgements. This work was supported by FP7 Marie Curie ITN transfer of knowledge programme under project PITN-GA-2013-606878-CERMAT2.

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Stable Regimes and Toruses of One Class of Impulsive Systems

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Let us consider a chain of 3 connected, singularly perturbed oscillators with a delay:

$$\dot{u}_j = d(a_1 u_{j-1} - a_2 u_j + u_{j+1}) + \lambda[-1 + \alpha f(u_j(t-1)) - \beta g(u_j)] u_j, \quad j = \overline{1, 3}, \quad (1)$$
where $u_j = u_j(t) > 0$, $a_1, a_2 \in \{0, 1, 2\}$, $\lambda \gg 1$, $\beta > 0$, $\alpha > 1 + \beta$ and smooth functions $f(u)$, $g(u) \in C^2(\square_+)$ have entry conditions: $0 < \beta g(u) < \alpha$, $f(0) = g(0) = 1$ and $f(u)$, $g(u)$, $u f'(u)$, $u g'(u) = 0(1/u)$, $u \rightarrow \infty$. There are researched 3 types of system (1) for different values of a_1, a_2 and conditions on u_0, u_4 : a) $a_1 = 1$, $a_2 = 2$, $u_0 = u_1$, $u_2 = u_4$; b) $a_1 = 1$, $a_2 = 2$, $u_0 = u_3$, $u_1 = u_4$; c) $a_1 = 0$, $a_2 = 1$, $u_1 = u_4$. In article [1] there was proved, when λ is sufficiently great, system (1) can be transformed to impulsive two-dimensional system without small parameters. Also for map

$$\Phi(z) : \begin{pmatrix} z_1 \\ z_2 \end{pmatrix} \rightarrow \begin{pmatrix} y_1(\tau_0, z_1, z_1) \\ y_2(\tau_0, z_1, z_1) \end{pmatrix}, \quad (2)$$

there was proved that exponentially stable points of map (2) are satisfied the orbitally, asymptotically stable cycles of system (1). In map (2) functions $y_1(t)$, $y_2(t)$ have entry conditions $y_1(-0, z_1, z_2) = z_1$, $y_2(-0, z_1, z_2) = z_2$. These functions are connected with initial variables by means of approximate equalities $y_1 \approx \ln u_2 - \ln u_1$, $y_2 \approx \ln u_3 - \ln u_3$. $T_0 = \alpha + 1 + (\beta + 1)/(\alpha - \beta - 1)$ is the first approximation of stable cycle of single oscillator of system (1).

The research of map (2) was implemented by means of special software, which used parallel independent streams on CPU. There are researched questions of existence and stability of periodic solutions depending on different values of initial parameters. Also the special attention is paid to the number of coexisting stable regimes. Some results of research were published in article [2].

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

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On the Symbol of Nonlocal Operators Associated with Actions of Discrete Groups of Diffeomorphisms

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The subject of this study is a class of nonlocal operators associated with actions of discrete groups of diffeomorphisms of smooth manifolds [1].

Namely, on an m -dimensional sphere \mathbb{S}^m we consider nonlocal operators generated by pseudodifferential operators (PDO) and shift operators along the trajectories of a parabolic diffeomorphism

$$g : \mathbb{S}^m \rightarrow \mathbb{S}^m, \quad x \mapsto x + e, \tag{1}$$

where is a $e \in \mathbb{R}^m$ nonzero vector. Such operators are represented in form of the finite sum

$$D = \sum_k D_k T^k : \quad H^s(\mathbb{S}^m) \rightarrow H^{s-d}(\mathbb{S}^m), \tag{2}$$

where $Tu(n) = u(n+e)$ is the shift operator corresponding to the diffeomorphism (1), D_k is a PDO of order d on the sphere \mathbb{S}^m , $k \in \mathbb{Z}$. The symbol of operator (2) is defined by the following expression

$$\sigma(D) = \sum_k \sigma(D_k)(x + ne, \xi) T^k : \quad l^2(\mathbb{Z}, \mu_{x, \xi, s}) \rightarrow l^2(\mathbb{Z}, \mu_{x, \xi, s-d}), \tag{3}$$

where $Tu(x) = u(x+e)$ is the shift operator of a sequence, and the space $l^2(\mathbb{Z}, \mu_{x, \xi, s})$ consists of sequences $\{u(n)\}$, $n \in \mathbb{Z}$, satisfying the inequality

$$\sum_n |u(n)|^2 \mu_{x, \xi, s} < \infty,$$

$\mu_{x, \xi, s}$ is the measure that was previously defined in paper [1].

As is known, the smoothness exponent s of the Sobolev space plays an important role in the elliptic theory of operators associated with actions of discrete groups of diffeomorphisms. The invertibility of symbol depends on this exponent. In the present paper, the following theorem is obtained.

Theorem 1. Let the symbol (3) be invertible for $s = s_0$, then it is invertible for all smoothness exponents of the Sobolev space.

In other words, it is proved that the ellipticity of the operator (2) doesn't depend on the smoothest exponent of the Sobolev space.

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Divergence of the Wing in the Supersonic Gas Flow Non-zero Equilibrium State and Local Dynamics

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Tasks of aeroelasticity plays fundamental role at designing wing of the aircraft. One of the important problem in this sphere is researching the static stability of the wing in the supersonic gas flow. Particular interest is a local dynamics of the phenomenon of the divergence of the wing. For researching this problems we used model of the flat wing. The torsion equation can be written in the next form [1]:

$$p_0 h \frac{\partial^2 \theta(x, t)}{\partial t^2} + p_0 h \gamma \frac{\partial \theta(x, t)}{\partial t} = G J_d \frac{\partial^2 \theta(x, t)}{\partial x^2} +$$

$$+ p_\infty \frac{(x_0 + b)x_0}{2} \left[\left(1 + \frac{\kappa - 1}{2} \theta(x, t) M_1 \right)^{\frac{2\kappa}{\kappa - 1}} - \right.$$

$$\left. - \left(1 - \frac{\kappa - 1}{2} \theta(x, t) M_2 \right)^{\frac{2\kappa}{\kappa - 1}} \right]$$

Boundary conditions is

$$\frac{\partial \theta(0, t)}{\partial x} = \theta(l, t) = 0$$

And by using the normal form approach [2] we got analytical results in three different cases

- 1) We found non-zero equilibrium states for $M_1^2 - M_2^2 \sim 1$;
- 2) Especially we researched the case of $M_1^2 - M_2^2 \sim \epsilon^{1/2}$;
- 3) And $M_1^2 - M_2^2 \sim \epsilon^{1/2}$ and $\gamma \ll 1$;

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Existence and Structure of Global B-pullback Attractors for Discrete-Time Cocycles Generated by a Class of Nonautonomous Control Systems with Perturbations

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In our talk a class of discrete-time nonautonomous control systems with perturbations is considered. The theory of cocycles (e.g., [1, 2]) is used for the investigation of such systems. For discrete-time cocycles a generalization of the well-known dissipativity lemma for dynamical systems ([3, 4]) is presented. Using this lemma and a frequency-domain condition we show the uniform dissipativity of our cocycle. This and the Kloeden-Schmalfuss theorem [1] allow us to prove the existence of the global B-pullback attractor for the given cocycle. We also investigate the structure of this attractor. We state that our attractor is represented by a unique bounded on the time set motion, which in a pull-back sense attracts all other motions of the cocycle. Furthermore we show that for a class of almost periodic perturbations and almost periodic in time nonlinearities in the generating nonautonomous control system the global B-pullback attractor for the cocycle is also almost periodic.

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Applying Machine Learning for DDoS Attacks Filtering. Analysis of CSIC 2010 Dataset

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The HTTP dataset CSIC 2010 [1] contains thousands of the http requests. It was developed at the “Information Security Institute” of CSIC (Spanish Research National Council) and could be used for detection, analysis and filtration of web attacks. The dataset was generated using the real data with all personal information removed. The dataset contains 36,000 normal requests and more than 25,000 anomalous requests. The HTTP requests are labeled as normal or anomalous and the dataset includes attacks such as the SQL injection, buffer overflow, information gathering, files disclosure, the CRLF injection, XSS, server side include, parameter tampering and so on.

The dataset was analyzed using different methods of machine learning, such as Random Forest, Support Vector Machine, Gradient Boosting, etc. The main idea of measuring algorithms efficiency is using cross-validation techniques: to split all the data into two parts, to train the model on the first part and to make predictions for the elements from another part and to check the suggestion.

Best results were shown by XGBoost Extreme Gradient Boosting with more than 97% accuracy. Next step of the research was anomaly detection (unsupervised learning): a model was trained using only information about normal request and there was no idea how anomalous traffic looked like. Accuracy, as expected, was lower than in the supervised learning. A model could be tuned up to reduce errors on the normal traffic, but it will mark more abnormal requests as normal. Also restricting a higher percentage of the anomalous traffic will lead to higher error rate on regular requests. The best results were shown by One-Class SVM with RBF kernel, some examples of error rates for different parameters are listed below.

Parameter “nu”	Parameter “gamma”	Errors train	Errors novel regular	Errors novel abnormal
0.09	0.1	18.272%	18.986%	17.179%
0.2	0.1	27.897%	27.8%	9.423%
0.03107	0.05414	10.467%	11.531%	27.696%

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Pattern Recognition and Prediction of Multivariate Time Series with Long Short-Term Memory (LSTM)

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Understanding and quantifying a dynamical system like air traffic management (ATM) at performance level is a challenging task. Performance Indicators represent states of captured, linked sub-systems, so the inner-workings of the system are recognizable shown in time-discrete time series [1]. For a valid prediction of the system behavior at performance level all correlations between the time series needs to be identified.

To overcome resulting complexities and dynamic effects the problem can be approached through advanced statistical procedures as LSTM are [2]. LSTM are advanced Recurrent Neural Network (RNN) structures, which are able to store information over time and capturing long-term dependencies without suffering from optimization hurdles through creating a multi-gate inlay (Fig. 1) [3]. A specially initialized and trained set of LSTM can predict a multivariate time series and consider the dependencies of all inputs and outputs.

The learned knowledge without having any expectations of the underlying processes allows to extract and solve (non-)linear, complex optimization problems with external inputs.

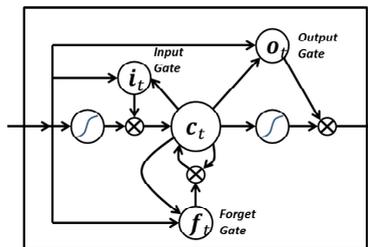


Fig. 1. A simple LSTM block with input, output and forget gates.

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Generation and Removing of Apparent Singularities in Linear Ordinary Differential Equations with Polynomial Coefficients

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During recent years, a number of publications have been devoted to investigation of the specific properties of ordinary differential equations with apparent singular points. In the present work we show that apparent singularities in the linear ordinary differential equations with polynomial coefficients can be generated via differentiation of equations and, vice versa, the integration of the equations containing apparent singularities may result in removal of these singularities.

We start with the ordinary differential equations with polynomial coefficients for which the highest degree polynomial stands in front of the highest-order derivative:

$$\sum_{k=0}^n P_k(z) \frac{d^{n-k} w(z)}{dz^{n-k}} = 0 \quad (1)$$

If the solutions of a linear differential equation in the vicinity of a finite singular point are functions of limited growth, then the singularity is of the Fuchsian type. The equations with Fuchsian singularities alone are referred to as Fuchsian equations.

Discussing several particular examples of Fuchsian equations, we show that, if the polynomial $P_n(z)$ standing in the last term of the sum in equation (1), that is, the coefficient in front of $w(z)$, adopts a zero at a finite point q of the complex plane, then the equation obeyed by the derivative of the solution of equation (1) in general involves an additional apparent singularity located at this point. Based on this observation, we formulate two conjectures of general nature concerning the generation and removing of apparent singular points in arbitrary Fuchsian differential equations with polynomial coefficients.

The Nonholonomic Bicycle Model as a Differential Inclusion

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Nonholonomic mechanics describes the motion of systems with nonintegrable constraints, i.e., constraints of the system velocities that do not arise from constraints on the configurations alone. These systems allow to consider a great variety of examples, which have a rotational motion component and are in contact with a surface [1]. The system we consider is an autonomous bicycle model of Getz [2] which is a representative case of a nonholonomic system.

In our talk the bicycle model with no friction is studied in the context of differential inclusions [3]. This allows us to use some modifications of the Takens embedding method for some class of differential inclusions with possibly discontinuous right-hand side. This realization is given in contrast to analytic embedding method in [4].

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D. Solid State Physics

Dielectric and Crystal Structure Study of the Ferroelectric Composites $(1-x)\text{NaNO}_2+(x)\text{BaTiO}_3$

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Ferroelectric composites belong to the inhomogeneous ferroelectric structures consisting of components with different dielectric properties. Macroscopic physical properties of similar systems can significantly differ from the properties of initial components due to mutual effects that allows to obtain materials with a desired set of properties that can be modified by varying the composition, the percentage of component, the degree of dispersion of the particles.

The results of complex research of powder mixtures $(1-x)\text{NaNO}_2+(x)\text{BaTiO}_3$ and at different concentrations of BaTiO_3 are reported. The dielectric studies of the composites have revealed some anomalies [1] of the dielectric response, for instance, additional maximum of dielectric permittivity at low frequencies besides the maximum at the Curie temperature of pure NaNO_2 . The goal was to clarify a nature of the observed low-frequency anomaly the dielectric response.

The study of temperature evolution of the crystal structure of the composites along with frequency analysis of complex dielectric permittivity allow to suppose the relation of dielectric response anomaly in the composites with processes of charge accumulation and resorption at the boundaries of BaTiO_3 particles.

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Secondary Electron Emission from Si_3N_4 and PMMA in Helium Ion Microscope

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Nowadays microelectronic devices tend to decrease their linear dimensions to the nanometer-scale. The main technique to produce the desirable device design is lithography. This technique based on the interaction of electromagnetic radiation or charged particles with the solid surface. Secondary electrons (SE), as well as primary particles, break bonds in the target and change its solubility in a solvent. Efficiency of this process depends on the parameters of SE emission, such as the yield of SE and the energy distribution of SE.

It was demonstrated that He ion beam allows to prepare sub-10 nm pattern that is noticeably better than with electron beam [1]. However, no data on SE emission from the resist materials are available up to now that are necessary to develop proper exposition procedure. In this work we investigated for the first time the energy distribution of the yield of SEs generated by helium ion beam.

Silicon nitride (Si_3N_4) and poly(methyl methacrylate) (PMMA) thin films on a silicon (Si) substrate were investigated with a helium scanning ion microscope Zeiss ORION at an accelerating voltage of 35 kV. The thicknesses of Si_3N_4 and PMMA films were 100-nm and 300-nm, respectively. A signal of SE was monitored by means of the Everhart-Thornley detector.

As Si_3N_4 and PMMA are insulators their surface becomes positively charged under the action of ions. As the result the electrons are attracted with the surface and SE yield decreases with increasing exposition time. To eliminate this effect and to obtain reliable data we developed special procedure consisting of the measurement of the dependence of SE yield on the distance between the points on the surface of the samples irradiated with the ion beam. In this way the proper experimental conditions were found corresponding to the absence of the interaction of electric fields of the points.

We used the method of retarding potential to obtain the energy distribution of SE. The semispherical grid was grounded and a positive potential was applied to the sample. It was established that the signal of SE decreases nonlinearly with increasing of retarding bias. The main fraction of SE has energy of about 1 eV.

Acknowledgements. Investigations were performed at the Interdisciplinary Resource Center for Nanotechnology (IRC-NT) of the Research park of Saint Petersburg State University.

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Plasmon-Induced Electrochemical Properties of Titanium Dioxide

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TiO₂-devices are perspective for photochemical decomposition of undesired impurities in the air and water and solar energy conversion [1]. However, the band gap of TiO₂ is ~3.2 eV. For this reason, TiO₂ is active only under ultraviolet (UV) light which is about 3-5% of the solar light reaching the earth surface. Incorporation of noble metal nanoparticles into semiconductor is a widely used strategy in searching for ways to increase the photocatalytic activity [2].

The gold loaded TiO₂ thin films were investigated by means of both the optical transmission spectroscopy (Fig. 1) and the photocurrent measurements (Fig. 2). Two types of Au-TiO₂ films, differing in Au nanoparticle allocation within the film 1) gold nanoparticles deposited on the film surface (Au_{surf}/TiO₂) and 2) gold nanoparticles distributed between two thin TiO₂ films (TiO₂/Au_{int}/TiO₂) were used. SEM, UV-VIS spectroscopy were applied for characterization. The difference in the positions of maxima of action spectra of the samples, related to Au nanoparticles plasmon resonance was revealed. This difference is probably due to the influence of the relative permittivity or/and the high refractive index of the TiO₂.

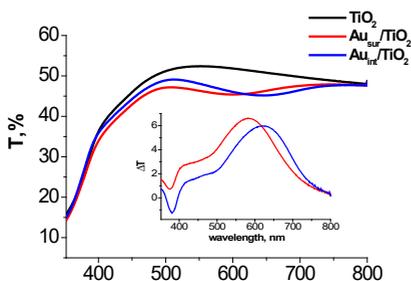


Fig. 1. Transmittance spectra of the Au/TiO₂ samples. Insert: Differences of diffuse reflection spectra.

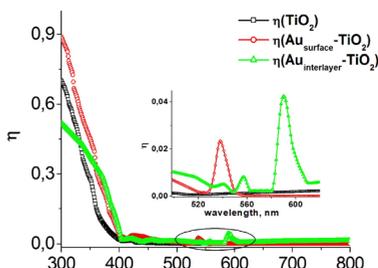


Fig. 2. The spectral dependences of photocurrent (TiO₂ (black), Au_{surf}/TiO₂ (red), TiO₂/Au_{int}/TiO₂ (green)).

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Photoinduced Adsorbo-Luminescence of Cr-doped MgAl₂O₄ Spinel

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The photoinduced adsorbo-luminescence effect is a luminescence flash, caused by dissociative adsorption of hydrogen-containing molecules on pre-irradiated surface of solid. This talk reports a comparative study of the luminescence of Cr-doped MgAl₂O₄ spinel induced by different excitation mechanisms: photoluminescence (PhL), thermoluminescence (ThL) and photoinduced adsorbo-luminescence (PhIAL) to understand the mechanism of PhIAL emission [1]. It would be very useful to show and separate possible ways of intrinsic and impurity defects excitation: free charge carriers transfer and direct energy transfer. Also it is important to separate surface processes, which influence on luminescence properties of the sample, because there is still no thorough understanding of mechanisms involved in PhIAL phenomenon. With this aim to mind, several experiments on registration of temperature dependences of photoluminescence and photoinduced adsorbo-luminescence were carried out. Thereby, the aim of present work is to classify, separate and control different processes, carried out during PhIAL effect.

Acknowledgements. The present study was performed within the Project “Establishment of the Laboratory “Photoactive Nanocomposite Materials” No. 14.Z50.31.0016 supported by a Mega-grant of the Government of the Russian Federation. 2.

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Local Atomic Structure of Copper Sites in Cu-MOR Synthesized by Solid-State Ion Exchange

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The direct conversion of methane to methanol from a practical point of view is a promising method for the direct production of methanol from natural gas, which permits low operating temperatures [1]. To solve such a problem different catalysts, including those based on copper zeolites, providing the methane selectivity of the oxidation reaction, are being developed [2, 3]. Identifying the distinct copper site that is active is a challenge since the Cu-zeolites used for the conversion of methane to methanol usually contain a variety of copper species, namely isolated ions, dimers, oligomers and particles [4, 5]. Depending on the method used for the synthesis one can obtain catalysts with different distribution of copper upon possible structural and charge states, which makes the definition of the atomic and electronic structure of the active sites in copper zeolites important task.

In present work the local atomic structure of Cu sites in Cu-MOR, synthesized by the solid-state ion exchange method using CuCl and H-MOR as precursors, was investigated by means of X-ray absorption spectroscopy in extended energy range (EXAFS). Interatomic distances Cu-O, as well as corresponding coordination numbers and Deby-Waller parameters are revealed. The dependence of the fraction of Cu ions in chloride upon the temperature of annealing is established.

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Structural Changes of Carbon-Supported Bimetallic PtCu Nanoparticles After Thermal Treatment by Means of SAXS and ASAXS

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Bimetallic platinum-copper nanoparticles on carbon support are studied as a perspective electrochemical catalyst by anomalous small-angle X-ray scattering (ASAXS) near the Pt absorption L_3 -edge as prepared PtCu/C

The particles are synthesized by simultaneous and sequential chemical depositions, as described in [1]. Experimental spectra were measured at mySpot beamline [2] at BESSY II synchrotron center (Berlin, Germany).

The data reduction and analysis were performed by GSAS-II code [3] modified for core-shell particles simulation. The results of simultaneous fitting of several diffraction patterns measured at different photon energies are illustrated in the Fig.1. Obtained size distributions after fitting are shown in the insets of the Fig.1.

The consideration of internal structure of the particles obtained by simultaneous or sequential depositions can be accounted through X-ray structure factors.

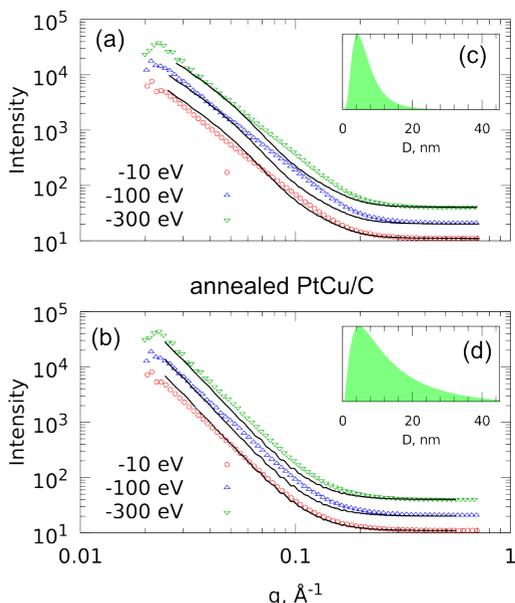


Fig. 1. ASAXS patterns of sequentially deposited particle (shifted for clarity).

The consideration of internal structure of the particles obtained by simultaneous or sequential depositions can be accounted through X-ray structure factors.

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Excitons in Low-Q Microcavities with Quantum Wells

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In this paper we consider the problem how strong interaction between light and exciton in the high-quality GaAs-based heterostructures can be. The relaxation time in a quantum well (QW) may show us possibilities of using these semiconductor structures in optical nanodevices. In order to strengthen the interaction between photons and excitons, we consider a 100-nm QW made of a InGaAs layer surrounded by GaAs barriers and placed in a low-Q (low-finesse) microcavity consisting of GaAs/AlAs layers. It was expected to observe a relatively narrow exciton resonance due to the heterostructure's high quality.

First of all, there were made simulations of reflectance spectra of the QW in the microcavity and the distribution of the light wave in the structure. Then we have experimentally studied reflectance and photoluminescence spectra of the sample grown by the method of molecular beam epitaxy at the SPSU research centre "Nanophotonics".

Experiments show no narrow exciton resonances in the reflectance spectra and presence such resonances in photoluminescence spectra. Therefore we plan to continue studying of the sample. At the same time, by comparing with results of experiment, the simulation data proved to be rather suitable (Fig. 1). For instance, positions of photon mode and edges of the photon stop-band are both similar.

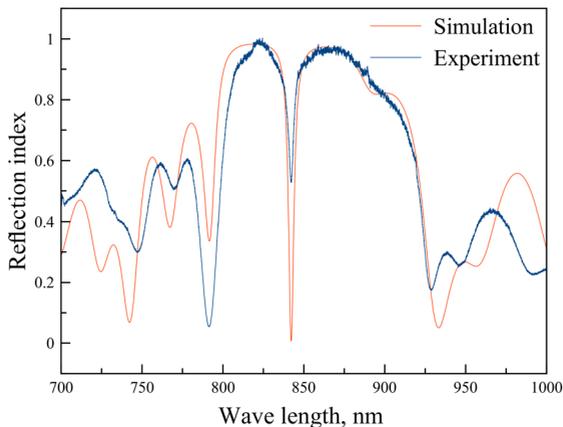


Fig. 1. Reflectance spectrum of InGaAs/GaAs QW in microcavity.

An Analysis of the High-Temperature Phase Structure of Multiferroic Solid Solutions of the PFW–PT

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The relationship between the electric and the magnetic subsystems in the multiferroic materials is manifested in the form of magnetoelectric effects. This allows using the electric field to control the magnetic properties, and, vice versa, adjust the electrical properties by the magnetic field. Examples include devices for modulating the amplitudes, the polarization and the phases of optical waves, optical diodes, spin wave generators, frequency conversion devices. [1]

PFW-PT $((1-x)\text{PbFe}_{2/3}\text{W}_{1/3}\text{O}_3 - (x)\text{PbTiO}_3)$ solid solutions are one of those materials and have the well-studied perovskite structure at high temperatures. Moreover, the recent dielectric studies have shown that at decreasing of PT concentration there is a crossover from the ferroelectric state to the relaxor behavior.

The temperature evolution of $(1-x)\text{PFW}-x\text{PT}$ crystal structure at $x = 0, 0.2, 0.3$ has been studied by neutron powder diffraction in the region of the morphotropic phase boundary (MPB), because compounds of this type are known to exhibit the most interesting macroscopic properties, such as high values of dielectric permittivity, piezoelectric response, electrostriction, etc., exactly in the MPB region.

The coexistence of cubic and tetragonal phases in the solutions with $x = 0.2, 0.3$ was found below $T = 259$ and 285 K, respectively. As a result of the data treatment, the atom coordinates, the occupation factors and the temperature dependences of cell parameters were determined in the cubic perovskite phase. It is well known [2] that the Pb ion is shifted from the high-symmetry position in the lead perovskite-type relaxors. Using the split-ion model we estimated the value of Pb static shifts (~ 0.1 Å) from their high-symmetry positions along the $[1\ 1\ 0]$ direction. It was shown that these shifts decrease with increasing the PbTiO_3 concentration.

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Vortex Dynamics in Nanocomposites with Embedded Superconducting BiSn Particles

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One of the most prespective directions in modern physics is the creation of new superconducting materials and technologies to use in micro- and nanoelectronics, mechanical engineering, magnetic technologies, electrical engineering, etc. One of the most important aspects in creating composite materials is the study of influence of various factors on material properties. For example, how conditions of confined geometry affect the temperature of phase transitions. Research in this area allows us to have more detailed information about the influence of different factors on material properties. Therefore, nowadays the scientific world focuses its attention on superconductivity in nanostructured metals. It shows new various features which are of interest for fundamental science. Recent studies of nanocomposites with small superconducting metallic inclusions have discovered new trend in transitions between states of different geometry, intricate phase diagrams. Besides, those nanocomposites represent another kind of structures which properties are influenced by size effects and particle-particle interactions. Such composites can be obtained by embedding metals into pores of various nanoporous silica matrices [1].

In this scientific work AC and DC magnetization measurements were carried out for a BiSn nanocomposite consisted of a metal-loaded porous glass with 18 nm pore size to study dynamics in the vortex system and H-T diagrams. Variations of AC magnetization with temperature and bias magnetic field were obtained at different frequencies and amplitudes of AC field. Activation barriers were evaluated from variations with frequency of the upper-temperature peak in χ'' (imaginary part of AC susceptibility) at different bias fields. The field dependence of the activation barrier followed the power law with exponents equal to 0.02 and 1.026 below and above 1200 Oe, respectively.

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Conductivity of ZnO Nanolayers Grown by ALD in MCP

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The unique possibility of conductivity measurement of ALD grown ZnO nanolayers in the MCP channel walls is presented. Taking in account that number of channels in MCP is about four millions, diameter of one channel is 5 microns and thickness of a plate is about 0,3 mm one can realized a measure of conductivity of a layer in width of 0,3 mm, length of 60 meters and height of one tenth nm.

Dependence of arbitrary resistance of ZnO layers grown by ALD on a thickness (number of cycles) at a fixed voltage of 100 V is $y = 648 x^{-2.4}$.

Evidently that dependence of the resistance of a layer on a thickness is not linear, especially in the beginning of a layer formation stage. In our measurements it formally presents by equation $y=648x^{-2.4}$ Therefor electro physical properties of ultra-thin layers of ZnO grown by ALD strongly dependent on a thickness of a layer. The main changes take place in the range of 10 monolayers. Subsequent layering produces a little change in the layer conductivity. Mobility of charge carriers' change the same way. Such dependence discussed in classic model of dimension effect and of quantum size effect.

Intercalation of Pb Atoms under Graphene on Ir(111) Monocrystal and Thin Ir (111) Film

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Graphene is a two-dimensional material with outstanding electronic and structural properties [1]. It has a unique honeycomb crystal structure, which symmetry causes the linear dispersion of the electronic states near to Fermi level. It means that the fermions close to the Dirac point (DP) have zero effective mass. Graphene had been expected to have incredible applications in nanoelectronics, but for this purpose, the band gap at the DP is required [1]. Recent works demonstrate the possibility of graphene application in spintronics and quantum computation. In this case spin-orbit interaction is desired to be enhanced in graphene, what can be realized by the contact with the heavy metals [2].

We have grown graphene by Chemical Vapor Deposition using the catalytic reaction of propylene cracking on Ir(111) monocrystal and Ir(111) thin film grown on Si(111) with an yttria-stabilized zirconia (YSZ) buffer layers. We study the electronic structure of graphene using angle-resolved photoemission spectroscopy (ARPES) with the application of synchrotron radiation. Surface crystal structure is investigated by low energy electron diffraction.

The main goal of present work is to study the variations of the graphene electronic structure on Ir(111) with intercalated Pb atoms. A number of theoretical works predict the giant enhancement of spin-orbit interaction in this system [3]. By means of ARPES we show the change of the graphene doping after the Pb intercalation. Moreover, depending on the Pb atoms locations the gap at the Dirac point is revealed. Owing to the absence of the shunting currents, we also use the Ir(111) thin film substrate for the system formation [4]. These results could open the opportunity for realizing of the topological phase in graphene and its spintronics applications.

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Magneto-Optical Faraday Effect in Microcavities

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Over the past few years the idea of creating optical computers becomes increasingly popular. It is supported on one hand by an inexhaustible desire for increasing computing speeds and, on the other hand, by the amazing possibilities of modern technologies. The spins of the charge carriers and the atomic nuclei are one of the promising systems for quantum information processing and possible framework for the creation of a quantum computer.

In this communication, we study the processes of build-up and decay of the nuclear spin magnetization by means of optical spectroscopy. In particular, the polarization of light interacted with spins of electrons in n-doped GaAs is analyzed. The slow and fast components of the nuclear spin relaxation are observed (Fig. 1). We analyze the characteristic times of these components allowing us to conclude the difference between the mechanisms of the nuclear spin relaxation in the vicinity of donor centers and in the area around them.

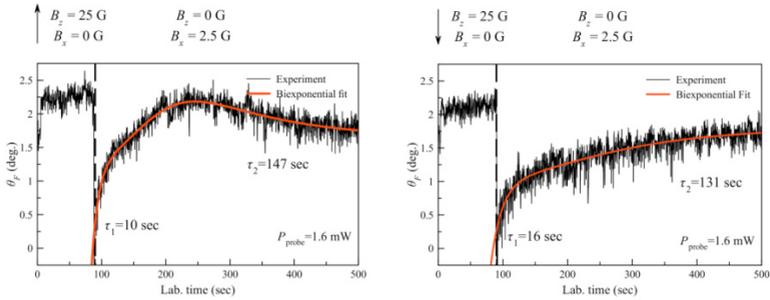


Fig. 1. The dynamics of nuclear spin relaxation in two different orientations of the longitudinal magnetic field.

Further study of the nuclear spin dynamics, especially its fast relaxation components, is necessary in order to implement in hardware the creation of quantum processing units and the all-optical cells of long-living nuclear spin memory.

NEXAFS Study of Cathode Material for Li-Ion Batteries During Charge and Discharge Processes

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Lithium-ion batteries (LIBs) are promising power supplies for use in electric vehicles. Traditionally, LiCoO_2 is used as a cathode material for LIBs. But using this structure leads to several drawbacks such as a poor structural stability, an extract all lithium ions and toxicity of cobalt. Therefore, it is important to develop alternative cathode materials.

One of the promising cathode materials for LIBs is $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ structure. This structure combines benefits for LiCoO_2 and LiNiO_2 such as structural cycling stability, higher capacity, improved safety and lower cost. The presence of Mn in the structure provides the cycling performance. Nevertheless, the detailed evolution of the local structure around the ions of metals and oxygen during one charge/discharge cycle is unclear up to now. In this connection the current work is directed to careful study of changes of local structure in the $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ structure during one charge/discharge cycle.

The analysis of Mn $L_{2,3}$ -absorption spectra shows that during the process of discharging the oxidation state of manganese is varied from Mn^{4+} to Mn^{3+} and back to Mn^{4+} for a completely discharged sample. Moreover, the similar situation was traced for cobalt, which also changes the oxidation state in the process of discharge from Co^{3+} to Co^{2+} and back to Co^{3+} for the full discharged sample. The greatest changes were found for nickel ions. It was established that pristine structure $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ is characterized by a mixed oxidation states $\text{Ni}^{2+}/\text{Ni}^{3+}$. During the charge process the oxidation state Ni^{3+} becomes dominant. But discharge process leads to the formation of the predominantly Ni^{2+} oxidation state.

Nevertheless, in the completely discharged sample the oxidation state of nickel coincides with the original structure. One can conclude that the presence of nickel in the structure provides a cycling stability of structure.

Formation and Magnetic Properties of Graphene-Capped Iron Silicide

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Unique electronic properties of graphene make it a promising material for various technological applications, especially in the field of spintronics and nanoelectronics. One of the most interesting tasks is integration of graphene with silicon-based technology. The promising approach is to use silicides for creation of semiconductor or insulating buffer layers between the graphene and the substrate. The aim of the present work was to study the intercalation synthesis of iron silicides underneath a single layer of graphene formed on a metal substrate and to investigate the magnetic properties of these silicides.

The experiments were carried out in the Russian–German Laboratory at BESSY II, Berlin and at the Resource Center (RC) “Physical methods of surface investigation” of Saint Petersburg State University under UHV conditions. At first, single-crystal 10 nm Ni(111) film with was grown on a W(110) surface. Then graphene was grown on the surface of a Ni film by chemical vapor deposition. Characterization of graphene was carried out by low-energy electron diffraction, PES with synchrotron radiation and angular-resolved PES. Finally, high-purity Fe and Si layers were sequentially intercalated under the graphene layer at 400°C. Magnetic properties of the films were studied by the magnetic linear dichroism (MLD) effect in the photoemission of Fe 3p electrons.

It is shown that the intercalation of Gr/Ni(111) with iron occurs over a wide range of coverage up to 14 ML. The graphene layer strongly interacts with the top-most Fe atoms and stabilizes the fcc structure of the film. The in-plane ferromagnetic ordering arises after the intercalation of 5 ML of Fe due to the thickness-driven spin reorientation transition. Subsequent intercalation of Gr/Fe/Ni(111) with Si leads to the formation of a patchy surface consisted of intercalated and nonintercalated areas. The intercalated islands coalescence occurs at 2 ML of Si when a Fe-Si solid solution covered with the Fe₃Si surface silicide is formed. The Fe₃Si silicide has an ordered ($\sqrt{3} \times \sqrt{3}$)R30° structure and demonstrates the in-plane ferromagnetic ordering. The obtained Fe₃Si silicide is reliably protected by graphene, making it compatible for nanoscale applications.

Acknowledgements. The study was supported by Russian Foundation for Basic Research (Project no. 16-02-00387), the Russian-German Laboratory at HZB-BESSY and the Resource Center “Physical methods of surface investigation” of Research Park of Saint-Petersburg State University (agreement on research cooperation no. S-RC-5/4).

Photoinduced Hydrophilic Behavior of Hydrated Surfaces of Composite Films based on TiO_2 and ZnO

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The photoinduced superhydrophilicity effect is a surface hydrophilic transition of some metal oxides in to superhydrophilic state under UV irradiation. Despite of wide practical application the understanding of mechanisms and reasons yielding the observation or non-observation of this effect on some metal oxide surfaces are still under discussion. It was suggested that reconstruction of hydroxy-hydrated water multilayer is occurred as a result of the photocarries trapping [1]. It would be very useful to determine which type of photocarries, photoholes or/and photoelectrons, rules the photoinduced hydrophilic conversion on the surface of certain material. In turn, knowing this type one can predict and create the surface with proper hydrophilic properties under light. Thereby, the goal of present work is to form the heterojunction structures based on TiO_2 and ZnO and to study the photoinduced hydrophilic transformations for such layer-by-layer films under UV light. Methods of optical tensiometry and the Kelvin probe were used. Alteration of water contact angles on the surface of composite films were also measured at applying of positive and negative potentials. It was found that photoinduced surface hydrophilicity of TiO_2 and ZnO thin films can be dramatically changed by creation of heterostructures.

Acknowledgements. The present study was performed within the Project “Establishment of the Laboratory “Photoactive Nanocomposite Materials” No. 14.Z50.31.0016 supported by a Mega-grant of the Government of the Russian Federation. A.Grishina and M. Maevskaya thank the Russian Foundation for Basic Research for financial support (No. 16-32-00341 mol_a).

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Near Field Induced Structuring of Photosensitive Polymer Films: SNOM and AFM Measurements

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Here we report on structuring of photosensitive polymer films by near field intensity pattern. The near fields were generated at a nano-groove fabricated within a thin metal layer. It is well known that when the nano-groove is irradiated, a surface plasmon wave is generated within the nano-groove, that as commonly expected should propagate along the metal surface. We have found, that instead of propagating SP mode, a standing EM-wave is generated at the metal/dielectric interface as a result of constructive interference between propagating SP mode and transmitted light. We have investigated two different sets of the nano-antennas consisting of either gold or silver thin films of 60nm in thickness patterned with nano-grooves of 100nm in width and 10 μ m in length using focused ion beam (FIB) technique and/or AFM nano-lithography.

We have analyzed this phenomenon using photosensitive azobenzene containing polymer film placed above the metal surface [1-4]. The polymer films deforms following the intensity distribution of light only in case of stationary distribution of the intensity or polarization pattern. We have analyzed the system theoretically and have found that the standing wave exist even in the absence of the polymer film. This was also supported by SNOM measurements [4].

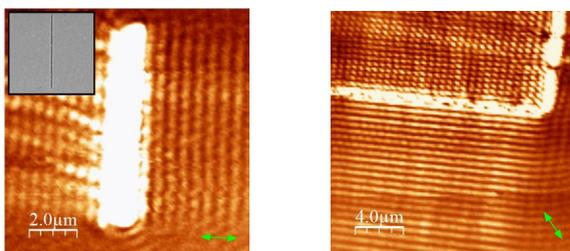


Fig. 1. Surface plasmons at a FIB nano-groove in silver (left) and at a nano-structure made by AFM nano-lithography (right).

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Effect of Non-Stoichiometry of the Ta₂O₅ on the Band Gap and Oxygen Vacancies Formation

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Resistive random access memory (RRAM), based on the filamentary resistance switching in an oxide layer sandwiched between two metal electrodes, has attracted attention as a promising candidate for next-generation non-volatile memory. Ta₂O₅/TaO_x structure has become a leading oxide layer in memory cells for RRAM due to good performance in many aspects (such as, high speed of resistive switching and stability of states). In a memory cell, oxygen vacancies are able to exchange between TaO_x and Ta₂O₅ layers upon applied voltage which results in controllable resistive switching.

According to [1], a Ta₂O₅/TaO_x structure can be controllably grown by combining atomic layer deposition (ALD) method with Ar⁺ ion beam irradiation. Formation of non-stoichiometry leads to changes in TaO_x properties. Therefore, it is important to study the effect of non-stoichiometry of TaO_x on the band gap and oxygen vacancies formation.

In the current work we study a non-stoichiometric TaO_x depending on x. The different stoichiometry of TaO_x was realized using in-situ Ar⁺ ion sputtering of the samples. The x-ray photoelectron spectroscopy (XPS) and the near edge X-ray absorption fine structure (NEXAFS) studies were performed after every step of etching. Thus, we were able to trace changes near the top of the valence band (VB) and the bottom of the conduction band (CB). NEXAFS spectra were measured using total electron yield in current mode. All the measurements were performed at RGBL-station on the Russian-German beamline at the BESSY II.

It was established that Ar⁺ ion sputtering allows to create a varying degree non-stoichiometric TaO_x accompanied by formation of a metallic Ta. The sputtering induced formation of metallic Ta may be important not only from the point of view of optimizing dry etching of the TaO_x films but, at the same time, may also be used to incorporate metallic particles or conducting layers into the Si/TaO_x-based heterostructures. The joined analysis of XPS and NEXAFS spectra points to the formation of the defect states above the top of VB with an increase in non-stoichiometry of TaO_x.

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Synthesis, Characterization and Upconversion Properties of ZrO_2 Doped with Rare Earth Ions

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The study of dielectric materials doped with rare earth ions for upconversion (UPC) of infrared radiation into shorter wavelengths attracts great attention due to possible photonics and biophotonics applications. It is known that doping metal oxides with rare earth ions leads to absorption in the extrinsic region [1]. Doping with pairs of rare earth ions can promote the observation of UPC in materials [2]. From the fundamental point of view, the process of UPC emission of rare earth ions in oxide nanocrystals and the way it changes with size, crystal phase and concentration is not well understood. Zirconia (ZrO_2) is an important photonic material for UPC studies because it is chemically and photochemically stable, has high refractive index and low phonon energy [3].

This work includes the synthesis, characterization and investigation of how the concentration of Yb^{3+} , Er^{3+} and Tm^{3+} ions affects the UPC properties of Yb^{3+} - Er^{3+} and Yb^{3+} - Tm^{3+} co-doped ZrO_2 nanocrystals.

Acknowledgements. The present study was performed within the Project “Establishment of the Laboratory “Photoactive Nanocomposite Materials” No. 14.Z50.31.0016 supported by a Mega-grant of the Government of the Russian Federation.

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Optical Properties of CdSe Quantum Dots Coated with Layer of ZnS

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Colloidal quantum dots (QDs) - semiconductor nanocrystals with size ranging 1-10 nm, consisting of 10^3 - 10^5 atoms. They are created by methods of colloid chemistry based on inorganic semiconductor materials in organic solvents. To prevent aggregation of QDs are used surface-active substance, for example triocetylphosphine oxide (TOPO) [1-2].

The interest in QDs caused by their distinctive physical properties, especially optical properties: the high quantum yield of photoluminescence (PL) and photostability, the wide absorption spectrum range and narrow band of the PL, the dependence of emission wavelength on the QD size [1-2]. In addition, the ability of the existence of the quantum dots in the form of colloidal solutions enables their introduction to the developed surface, extends the ability to create composite materials [1].

In present work we use colloidal CdSe/ZnS (Core/Shell) QDs covered with TOPO, deposited on different semiconductor surfaces (CdSe, GaAs, GaAs nanowires, Si). ZnS «shell», formed around CdSe «core», as a passivator of surface states and as localizer of electron-hole pairs in the nucleus increases significantly the quantum yield of PL [1]. We investigated the PL of the samples at $T = 293$ K and different atmospheric pressure. Quantum-shift was determined from the luminescence spectra of QDs on the surface of single-crystal CdSe, this allowed to define size of the QDs. The character changes PL of QDs with time was obtained at atmospheric pressure and vacuum. Has appeared that the optical properties of the system change after extracting QDs from liquid to the surface of the semiconductor. We suggest that the observed effects are due with the appearance of surface states as a result of oxidation of ZnS when interacting with the atmosphere.

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Photo-Induced Alteration of Hydroxyl-Hydrate Layer on TiO₂ and ZnO Surfaces

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The effect of photoinduced superhydrophilicity has a great practical importance in the creating of self-cleaning and anti-fogging coatings [1]. But the question about its mechanisms is still open for discussion.

In the present study photoinduced alteration of hydroxyl-hydrate cover on TiO₂ and ZnO surfaces was explored by different methods: optical tensiometry, FTIR spectroscopy, UV-Vis-NIR spectroscopy. Also quantum-chemical calculations for titanium dioxide and zinc oxide nanoclusters by DFT method were carried out.

Optical tensiometry results showed that hydrated TiO₂ surface becomes superhydrophilic under UV irradiation. Hydrated ZnO surface cannot reach the superhydrophilic state neither under UV nor visible photoexcitation.

UV irradiation of hydrated TiO₂ sample results in the distinct increase of the amount of water molecules coordinately bounded to superficial Ti cations. The presence of gaseous oxygen amplifies this effect. Irradiation by visible light reveals the increase of the amount of water molecules in the outer adsorption layer. Diffuse reflectance UV-Vis spectroscopy indicates the change of the amount of the electron and the hole surface centers after the sample photoexcitation. The effects of UV and visible irradiation are diverse.

UV irradiation of strongly hydrated ZnO sample reveals that desorption of water molecules from the surface is occurred. To the contrary, the irradiation by visible light results in the increase of the amount of adsorbed water molecules. The amount of the electron and hole surface centers remains intact after sample irradiation. Hence, different changes in hydroxo-hydrate water multilayers of TiO₂ and ZnO samples take place after the same irradiation. The effect does depend on the spectral composition of acting light.

Acknowledgements. The authors are grateful to RC "Nanophotonics", RC "Nanotechnology", RC "X-ray Diffraction Studies", "Thermogravimetric and Calorimetric" RC of the Research Park at the Saint-Petersburg State University for the experimental and technical support.

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IXMCD-Study of Shiral Magnets

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Exotic spin-structures like helical magnetics, spin glasses, low-dimensional magnetic materials play an important role in condensed matter physics. Physical properties of these materials are determined by various interactions. The existence of a strong isotropic exchange interaction along with weak relativistic interactions destroying spin symmetry, lead to complex magnetic structures and new phenomena - the emergence of long-period chiral spirals, the emergence of "skyrmions lattices", complex phase transitions with multiple order parameters [1]. External forces can easily break the balance caused by these interactions: pressure, magnetic field and etc [2]. That's why these structures are of special interest.

XMCD-spectroscopy is the powerful method for studying magnetic properties with X-rays. Its element selectivity is the most important advantage. All the measurements were performed on ID12 beamline at the ESRF (Grenoble, France). We have study K-edges of MnGe polycrystalline sample and FeGe single crystal. The difference between Mn and Fe XMCD-spectra can be explained by additional interaction in MnGe system (Fig. 1).

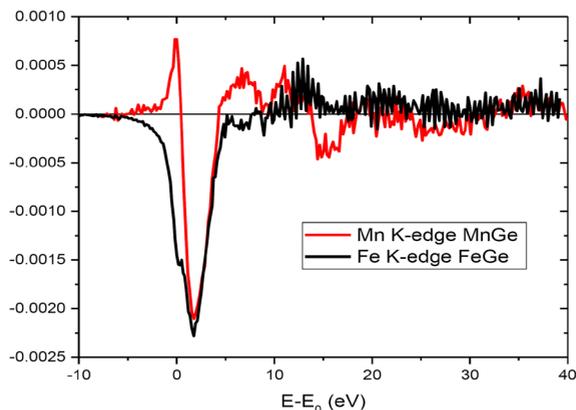


Fig. 1. XMCD-spectra of Mn and Fe K-edges.

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Study of Chemical Phase Composition of Multilayered Structures Si/TiN/(Al₂O₃)TiO₂/HfO₂ Using Hard X-ray Photoelectron Spectroscopy

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With decreasing of topological size of MIS (MIM) structures the role of processes at interface between metal and insulator, such as interdiffusion and chemical reaction significantly increases. As a result can forming thin layers in interphase boundary. Such interlayers directly impact on the functionality of the devices, for example, critically determines the effective work function. The problem can be solved by inserting thin interlayers at metal/insulator interface.

The technologically important system TiN/HfO₂ was chosen for our investigations. This structure actively applies in advanced logic and memory semiconductor devices and is of great interest.

The work is focused on the investigation of atomic and electronic structure of the interface between metal electrode TiN and active layer HfO₂ and opportunity to effect on its composition and extension by inserting of thin layer of other chemical composition (Al₂O₃ or TiO₂).

X-ray photoelectron spectroscopy of high kinetic energies (HAXPES) was used to examine the depth profiles of the structures. The depth profiling of the samples was realized by changing the emission angle of photoelectrons at fixed exiting photon energy. It was established:

- The oxidation of TiN electrode occurs in the system HfO₂/TiN with formation of TiNO and TiO₂.
- The insertion of Al₂O₃ thin layer restricts to some extent the interdiffusion in this system.
- When TiO₂ is inserted the formation of TiNO is smaller than in HfO₂/TiN/Si system, but more than in the system HfO₂/Al₂O₃/TiN/Si.
- In all the studied systems the active layer HfO₂ is uniform in depth.

Local Electronic Structure and Nanolevel Hierarchical Organization of Bone Tissue

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Bone is a complex hierarchical biomaterial which consists of two main components: organic matrix and mineral matrix. We will make an emphasis on mineral matrix, which is built out of mineralized plates separated by collagen fibrils. The plates, in turn, are formed by solid crystallites of hydroxyapatite ($\text{HAP} = \text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) and hydrated layers which are adsorbed on crystallite surface.

Presence of hydrated layers and their interaction with nanocrystallites are of great importance for many biological processes and properties of bone tissue both mechanical and bio-chemical [1]. For this reason, development of a model for atomic and electronic structure of bone tissue was the aim of present work. The resulting 3D superlattice model was successfully applied in order to predict certain features of electronic structure of bones and the prediction was confirmed by means of NEXAFS spectroscopy.

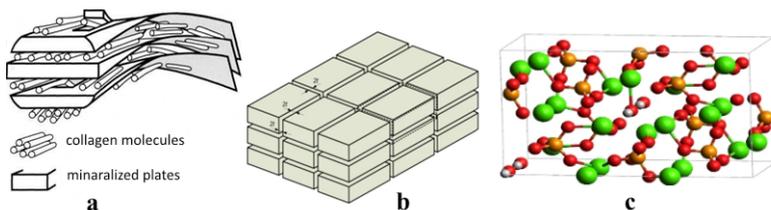


Fig. 1. Levels of hierarchical organization of bone tissue: a - mineralized plates distributed along collagen molecules; b - the coplanar assembly of the nanocrystallite; c - the crystallographic rectangular cell of HAP.

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Local Electronic Structure and Hierarchical Organization of Bone Tissue: Theory and NEXAFS Study

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Bone is a complex hierarchical biomaterial which consists of two main components: organic matrix and mineral matrix. We will make an emphasis on mineral matrix which is built out of mineralized plates separated by collagen fibrils. The plates, in turn, are formed by solid crystallites of hydroxyapatite ($\text{HAP} = \text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) and hydrated layers which are adsorbed on crystallite surface. These layers are basically water solution of Ca and P ions. Presence of water is of great importance for many biological processes and properties of bone tissue both mechanical and bio-chemical [1].

The aim of present work was to develop in vivo model which takes into account modern medical and biological research for description of atomic and electronic structure of bone tissue. The developed model was applied for investigation of electronic structure of bones and results were verified by NEXAFS analysis of native bone, dried bone and bone tissue building materials samples.

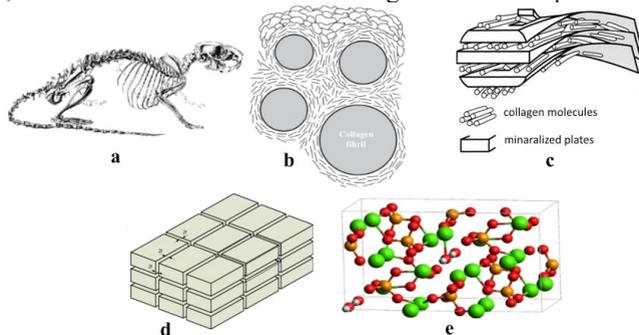


Fig. 1. Levels of hierarchical organization of bone tissue. a – rat skeleton; b - macrocomposition of nanocrystallite assemblies around fibrils in bone tissue, c – mineralized plates distributed along collagen molecules; d - the coplanar assembly of the nanocrystallite; e - the crystallographic rectangular cell of HAP.

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Ab initio Insight into O₂ Adsorption on TiO₂ Surface under Dark and UV Irradiation Conditions

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We present DFT study on O₂ adsorption on the defect TiO₂ surface which is modeled via amorphous Ti₈O₁₆ nanocluster. Open-shell singlet (OS) and triplet (T) electronic states of the cluster mimic excitation of the dioxide upon UV irradiation, while its closed-shell (CS) singlet state simulates unilluminated TiO₂. Only one adsorption site of Ti₈O₁₆ is considered. In the case of the OS singlet and the T states it is Ti³⁺ center. In the CS singlet case it is Ti⁴⁺. The calculations predict formation of two physisorption complexes - [Ti₈O₁₆^{CS}·O₂] and [Ti₈O₁₆^T·O₂] and the chemisorption complex [Ti₈O₁₆^{OS}·O₂]. The latter exists in two isomeric forms - with lateral or axial O₂ orientation. The lateral isomer can be transformed into axial one that results in -0.36 eV energy gain and proceeds through a barrier of 0.38 eV. Relative energies of the complexes with respect to energetically most favorable [Ti₈O₁₆^{CS}·O₂] are 0.46 eV [Ti₈O₁₆^{OS}·O₂]^{lateral}, 0.82 eV [Ti₈O₁₆^{OS}·O₂]^{axial}, and 1.58 eV [Ti₈O₁₆^T·O₂]. The physisorption complexes are characterized by low standard adsorption enthalpies ($\Delta H^0 \sim -0.4$ eV) and large Ti-O distances ($r = 2.4$ Å) as compared to the chemisorption complexes ($\Delta H^0 < -1.7$ eV; $r < 2.0$ Å). The obtained *zz*-components of *g*-tensor of O₂ in [Ti₈O₁₆^{OS}·O₂] isomers differ significantly that can be used for verification of experimentally observed O₂ adsorption patterns. The latter can not be determined unambiguously based on the energetics of O₂ adsorption alone.

Search for a New Short-Range Interaction by Neutron Scattering Technique

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There are four known fundamental forces in nature. However, the existence of new interactions is extensively discussed in the literature. One can recognize several methods of searching, and one of them can be carried out by the means of neutron scattering.

A new idea of experiment - neutron scattering on silicon powder – can be proposed. Estimations of coupling constant are calculated. It is shown that new experiment can improve current constrains by two exponents on the scales of interaction of 10^{-12} – 10^{-10} m. It is found out that the experiment can be done on existing powder diffractometers (for example, D2B in Institute Laue-Langevin); it allows to hope for realisation of proposed method in future.

EXAFS Study of Atomic Structure of Bimetallic Nanoparticles in PtCu/C Electrocatalysts before and after Thermal Treatment

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Composite materials containing noble metal nanoparticles are extensively synthesized and studied because they exhibit valuable functional characteristics, being highly efficient catalysts towards oxygen electroreduction and hydrogen electrooxidation [1, 2]. Nanocatalysts PtCu/C with core-shell structure of PtCu nanoparticles were synthesized by the method of simultaneous chemical reduction of Cu²⁺ and Pt(IV) in carbon suspension, prepared on the basis of ethylene glycol–water solvent. The characterization of atomic structure of as prepared PtCu nanoparticles and obtained after thermal treatment at different temperatures in range between 200 °C and 350 °C, was performed by Pt L₃- and Cu K-edge extended X-ray absorption fine structure (EXAFS) using the technique for determining local structure parameters of the absorbing atoms, which have the nearest surrounding consisting of Pt and Cu atoms [3, 4]. The spectra were measured at the μSpot beamline of the BESSY-II Synchrotron Radiation Facility (Berlin, Germany).

EXAFS spectroscopy is one of efficient methods for the study of nanoparticles because of its sensitivity to local atomic structure and composition, high spatial resolution and applicability in absence of long-range order. Meanwhile, EXAFS derived values of parameters for the nearest neighbors of absorbing atoms in bimetallic nanoparticles enable to make only indirect conclusions on the atomic structure of the studied nanocatalysts. To determine the relationship between the synthesis or treatment conditions – atomic structure – electrochemical performances of these materials, it is necessary to visualize the character of components distribution over the volume of nanoparticle, in correspondence with the values of structural parameters derived from EXAFS.

3D modeling of the atomic structure of bimetallic nanoparticles in PtCu/C electrocatalysts was performed by simulations of the atomic clusters, which correspond to the values of the local atomic structure of Pt and Cu atoms derived from EXAFS [5]. These models enabled to reveal the relationship between temperatures of thermal treatments and components distributions over the volume of PtCu nanoparticles in the studied electrocatalysts.

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Application of the Method of Hydrogen Permeability to Determine the Terminal Solid Solubility of Hydrogen in Ti-Alloys

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Currently the problem of hydrogen interaction with structural materials is quite acute. This problem is particularly acute for the hydride-forming materials, such as Ti and Zr. Titanium alloys are widely used in medicine, military industry, chemical reactors, high-vacuum pumps and pipelines. In addition, titanium alloys are the most important structural material in aircraft and rocket production. Both titanium and zirconium tend to accumulate hydrogen forming hydride phase, which leads to hydrogen embrittlement and decrease in the mechanical strength. To predict the behavior of titanium alloys contacting with hydrogen during the hydrides formation it is necessary to determine the temperature dependence of the terminal solid solubility of hydrogen in the alloys.

To determine the terminal solid solubility of hydrogen it is possible to use the method of hydrogen permeability. This method has been previously applied to zirconium alloy E-110. In this paper, the method of hydrogen permeability is used to determine the terminal solid solubility of hydrogen in titanium.

A Change of the Charge State of the MIM Structures Due to Resistive Switching

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Investigation of a change of the charge state of oxide dielectrics due to resistive switching has been made. Al-TiO₂-Si and Al-TiO₂-SiO₂-Si structures were investigated. Obtained volt – current characteristics showed forming process and resistive switching. High-frequency volt - capacities characteristics provided changes of the charge state of previously mentioned materials. Analysis of the results reveals certain patterns and possible mechanisms of corresponding changes of a charge state of the investigated structures.

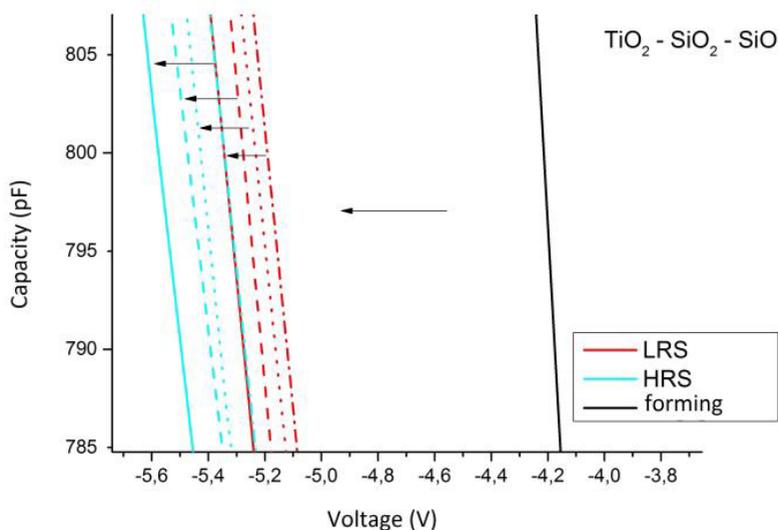


Fig. 1. VC-curve of resistive switching

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Comparative Study of NEXAFS Spectra of NiTPP and CoTPP Complexes: Role of Exchange 3*d*-3*d* Electron Interaction

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Various 3*d*-metal porphyrins (3*d*-MPs) have a lot of technological applications in such fields like molecular electronics, non-linear optics, catalysis, cancer diagnostics and therapy, sensory and many other [1]. Because of this their electronic structure has been a subject of numerous experimental investigations. The aim of this work was to compare M 2*p* and M 1*s* NEXAFS spectra of Ni and Co tetraphenylporphyrin complexes (NiTPP and CoTPP) in order to find out the influence of the exchange interaction between 3*d* electrons in unfilled MOs on the fine structure of M 2*p* and 1*s* absorption spectra of CoTPP.

M 2*p*, N 1*s* and C 1*s* X-ray absorption spectra were acquired using facilities of the Russian-German beamline at the BESSY II [2] and M 1*s* spectra were measured using equipment of the Structural Material Engineering endstation at the Siberia-2 storage ring at the Kurchatov Synchrotron Radiation Source [3]. Samples for investigation were porphyrin powders poured into thin cell in the case of M 1*s* spectra and thin porphyrin layers on the various metallic substrates in the case of M 2*p*, N 1*s* and C 1*s* spectra. M 1*s* absorption spectra were acquired with transmission method using ionization chambers as detectors of X-ray radiation. M 2*p*, N 1*s* and C 1*s* spectra were measured using total electron yield mode by detecting the sample current.

Comparative analysis of the M 2*p* and 1*s* absorption spectra of the NiTPP and CoTPP complexes showed that exchange 3*d*-3*d* electron interaction reveals itself in the M 2*p* and M 1*s* X-ray absorption spectra as a result of an appearance of the singlet and triplet final states of X-ray absorption transitions.

Acknowledgements. This work was supported by the RFBR (Grant no.15-02-06369).

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Evolution of Diffuse Scattering of Single Crystals $\text{Sr}_{0.6}\text{Ba}_{0.4}\text{Nb}_2\text{O}_6$

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Crystals of solid solutions $\text{Sr}_x\text{Ba}_{(1-x)}\text{Nb}_2\text{O}_6$ (SBN $_x$, $0.2 < x < 0.8$, *P4bm*) belong to uniaxial relaxors [1]. At increasing Sr concentration the phase transition temperature decreases [2] with the simultaneous enhancement of relaxor behavior; i.e. the diffuseness of the dielectric permittivity (ϵ) maximum becomes more pronounced and the frequency dispersion of $\epsilon(T)$ increases.

In the recent years the critical behavior in SBN60–SBN61 crystals is under discussion. We have carried out the study of diffuse scattering near the (002) and (220) sites at zero applied electric field [3]. In vicinity of (002) Bragg peak we have observed an intense scattering, which strongly depended on the temperature and on the applying of the electric field. It has been shown that below the Curie temperature the correlation length remains constant and approximately is equal to 27 nm. We also determined the critical exponents $\nu = 0.67(2)$ and $\gamma = 1.33(17)$ and Curie temperature $T_C = 340.5(1.2)$ K.

However the spatial distribution of diffuse scattering and effect of applied electric field remain practically unclear. We have carried out the study of temperature evolution of diffuse scattering in SBN60 single crystal at zero field and at applied electric field. So we find out that applying of external electric field suppresses scattering on configuration fluctuations.

In its turn the work carried out at room temperature revealed that the diffuse scattering consists of two components - the scattering described by a Lorentzian, and scattering described squared Lorentzian, each of which correspond to two different correlation lengths in the directions [110] and [001].

This work gives the possibility to obtain the information concerning to spatial organization of the order parameter fluctuations in this crystal near the phase transition temperature.

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Combined Investigations of Optical and Electrical Properties of Regular Dislocation Networks in Silicon

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The idea to construct all-Si LED exploiting the D1 dislocation-related luminescence in Si as a light source with 1,5 μm wavelength for on-chip interconnection promises a lot of advantages for the novel computer technology [1-3]. Especially, these experiments were promoted by development of the Si wafer direct bonding technique [4] allowing the well-controllable fabrication of dislocation networks (DN) with predefined dislocation density, types (screw and/or 60° dislocations), located at a suitable depth under the wafer surface.

During previous investigations, the non-monotonic behavior of D1 luminescence intensity with increase of twist misorientation angle was found, showing the existence of an optimum twist angle around 3° which provides the highest intensity of D1 luminescence [2]. However, the exact reason for such non-monotonic behavior of luminescence intensity was not clarified in the early articles.

In this work we present the results of extensive deep level transient spectroscopy (DLTS) investigations performed on a set of p-type Si bonded samples prepared with different twist misorientation angles focusing on the establishment of the correlation between the electronic and luminescence spectra of dislocation networks. We have found a big difference between the DLTS spectra measured on bonded samples prepared with twist angle below and above 3° : the low-temperature peak due to shallow traps dominating on spectra of samples with angle $<3^\circ$ starts rapidly decrease and finally disappears in samples with angle $>3^\circ$, and simultaneously the unsymmetrically broadened peak due to the deep traps starts to grow. The properties of these deep traps were studied on Accent DLTS spectrometer with precise voltage source installed in IHP Microelectronics (Frankfurt-Oder, Germany).

By comparison of DLTS spectra with photoluminescence data the linear increase of D1 luminescence intensity with density of shallow traps was revealed, whereas the deep traps provide rather a non-radiative recombination channel. Detailed discussion on the obtained results will be presented at the Conference.

Acknowledgements. This work was partly funded by G-RISC project p-2016-a-18.

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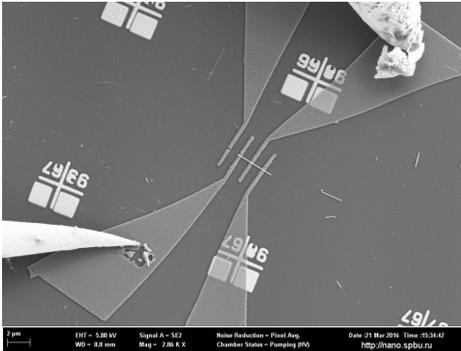
Electrical Characterization of Semiconducting Nanowires

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At the present time, a lot of scientists are greatly interested in researching of semiconductor nanowires due to their potential application in novel nanoelectronic devices, such as nanotransistors, gas sensors, etc [1]. Nanowires are the semiconducting structures with enhanced surface-to-volume ratio, so that the surface states would have a considerable influence on their conductivity properties. Therefore it is very important to find the experimental method suitable for nanowire surface states characterization. For this purpose we suggest the application of deep level transient spectroscopy method working in the current mode as well as photo-induced current transient spectroscopy (PICTS) method.

However, before immediate application of the suggested techniques, the problems with the formation of electrical contacts towards the nanowire have to be solved.



In this work we will describe the details of the developed contacting procedure by the method of electron beam nanolithography and present our first results of current-voltage measurements on GaN nanowire located on the silicon oxide substrate – see Fig. 1. Performed current-voltage measurements allowed us to define the carrier concentration of the nanowire under investigations.

Fig. 1. SEM image showing the GaN nanowire lying on isolating silicon oxide substrate together with the Ti electrical contacts and sticks of the micromanipulators connected with the microampere meter.

More details about the obtained results together with the extensive description of the suggested surface state characterization methods will be presented at the Conference.

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Spectral Investigation of Fluorine-Doped TiO₂

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Titanium dioxide is one of the most commonly used photocatalysts for a wide variety of reactions, because of its high activity in degrading many organic and inorganic pollutants. The characteristic fundamental absorption of TiO₂ lies in the UV region ($\lambda \leq 400$ nm). This practically rules out the use of sunlight whose UV fraction is extremely small. The sensitization of TiO₂ to longer wavelength radiation is a very actual problem. It is worth mentioning that sensitization of TiO₂ to visible light would allow about 40% of solar energy to be utilized. Main approach is used to introduce active sites in or at the surface of TiO₂ able to absorb visible light. It includes doping, codoping, grafting, sensitization by dyes, deposition of nanoparticles with localized surface plasmon resonance, etc. However, an increase in the optical absorption does not mean an increase in the photocatalytic activity.

The aim of our work is the experimental studies of the alteration of photo-activity of TiO₂ caused by fluorine doping. Tested samples were F-doped TiO₂, with concentrations of fluorine 0.5 and 2 wt%, and pristine TiO₂ as a reference sample. Samples were prepared by flame spray pyrolysis and sol-gel precipitation techniques. All samples were characterized by standard methods such as XRD, XPS and BET.

We have studied the activity of F-doped TiO₂ with respect to hydrogen, oxygen and methane photoadsorption. As major results, the influence of photostimulated adsorption of donor and acceptor gases on defect formation has been demonstrated.

We have measured spectral dependencies of quantum yields of photostimulated adsorption of hydrogen, oxygen and methane on F-doped samples with 0.5 and 2 wt% as well as on pristine TiO₂. Electrochemical study of the spectral dependencies of the photocurrents on the same samples has also been performed. Obtained results have been compared with the quantum yield dependencies of hydrogen and oxygen adsorption.

Acknowledgements. This work was supported by a Mega-grant of the Government of the Russian Federation (№ 14.Z50.31.0016). The authors are also grateful to Resource Center “Nanophotonics” of SPSU for the experimental and technical support.

F. Optics and Spectroscopy

Magnetite Spherical Nanoballs: towards Magnetic Photonic Crystals

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PCs are periodically ordered structures (single, two or three dimensional) made of materials with different refractive indices. The periods of such superstructures are comparable with the wavelengths of incident electromagnetic radiation in the optical range [1]. Due to existence of energy gap, it is possible to modulate propagation of light within periodic lattice and to control formation of the optical effects such as Bragg reflections. One of the most promising areas for development in this field is a creation of systems with possibility to change its lattice parameters under influence of external stimuli, for example, by application of magnetic field.

In this work, synthesis of magnetic photonic crystals (MPC) is described. The MPC were synthesized by simple solvothermal method. Produced MPC are magnetic nanoballs consisting of magnetite nanoparticles and citrate residues as a stabilizing agent. By controlling the synthesis conditions (e.g., used reagents, ratio of chemicals, etc.), different size of MPCs spheres ranged between 100 -150 nm could be obtained with a narrow size distribution. The obtained Fe_3O_4 nanoparticles show spherical shape with superparamagnetic property. Optical properties of MPC water colloid solution, such as transparency and spectra of a reflected light can be manipulated by application of external magnetic field.

Such monodispersed Fe_3O_4 nanoclusters can be used to produce magneto-optical systems for needs of optics and in fabrication of microelectronic devices.

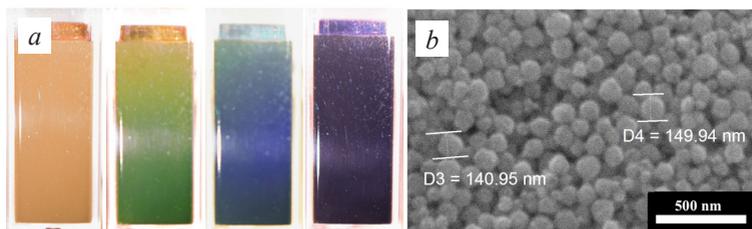


Fig. 1. Optical photos of the MPC based liquid showing different colour response after applying external magnetic field (the magnet–sample distance decreases gradually from left to right) (a); SEM image of magnetic photonic crystals (b).

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Excited Xenon Clusters and their Relaxation Processes

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Photoionization studies of clusters of atoms or molecules offer unique insight into the evolution of the electronic structure bulk solids from their constituent atomic/molecular building blocks. Photoelectron spectroscopy provides a suitable means to study rare gas clusters due to the short interaction time of the photoelectron with the residual cluster ion.

In the paper [1] this method was used to study the relaxation processes of the xenon clusters excited electronically by multi-photon absorption of laser radiation. It was shown, that two different relaxation processes occur.

Registration of fast and slow electrons reflects two distinct decay channels of excited clusters Xe_N^* . These processes are schematically shown in Fig. 1. The first process is accompanied by desorption of the excited atoms Xe^* in various states and their ionization by the next photon. The left part of the figure contains a diagram of the energy levels for atoms Xe^* (E_a) and ions Xe^+ . Based on this diagram, it is easy to explain the creation mechanism of electrons with the energy of 1.5–4.5 eV. The second process corresponds to two-photon ionization of clusters.

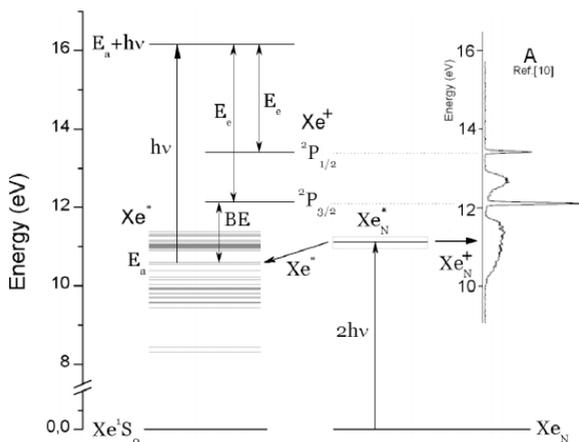


Fig. 1. The relaxation channels of two-photon excited Xe_N clusters.

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Methane Spectrum Interference Filter Based on the Fresnel Lens

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Of many problems on air pollution by different molecular gases, the detection and measurement of concentration of the greenhouse gases remains actual for years. In this paper, we concentrate ourselves on the problem of detection and tracing of small concentrations of Methane. Optical revealing of small concentration of any gaseous component in the atmosphere needs in very effective methods of measurement of faint emission or weak absorption of light. In [1] we suggested a new vision of the solution of general problem of detecting and measurement of small or even vanishingly small concentrations of impurities in some bulk matter using spectral analytical methods. In the accord to our estimates, the new approach can increase the sensitivity of spectroscopic methods of determination of gaseous components at least one order of magnitude in comparison to the traditional methods of registration.

The data given in our paper obviously show the great potential of engineering of special filters aimed on detection some molecules of pre-selected type in gas phase, including the atmosphere of our Earth. We have demonstrated that the general idea of accepting the emission corresponding to the complete vibrational-rotational or pure rotational spectrum band can be realized using multibeam interference optical system in the form of Fresnel lens or Fresnel reflector, no matter whether the emission or absorption is measured. According to theory, by using of those simple devices, one can expect the increase of sensitivity at least an order of magnitude under all other comparable to existing systems parameters.

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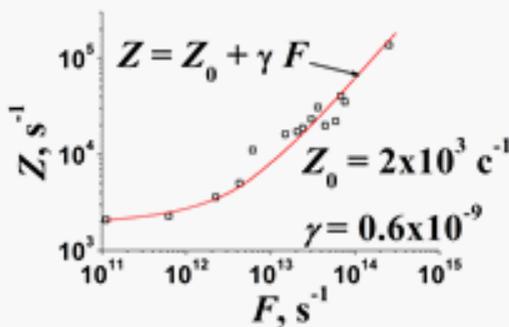
Effect of Visible-Spectrum Light on the Breakdown in a Long Discharge Tube

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The work is devoted to investigation of poorly studied effect of the visible-spectrum light on the electrical breakdown in a long discharge tube.

Measurements were performed in a tube filled with neon at a pressure of 1 Torr. The tube was of 80 cm length and 18 mm i.d. Breakdown was produced with rectangular pulses with the voltage of 1 kV, the repetition rate of 0.2 Hz, and the pulse duration of 10 ms. The area around the high voltage anode was illuminated by the LED ($\lambda = 460$ nm) or the laser module ($\lambda = 407$ nm). The light flux was varied from 10^{11} to 10^{16}



photons per second using optical filters. For each light flux *Fig. 1. Dependence of Z value on the photon flux.*

720 measurements were performed.

An interval between the pulse leading edge and the current appearance (breakdown time delay, t_d) includes statistical delay t_s (time waiting of effective electron appearance) and formative delay t_f (time for avalanche development), so that $t_d = t_s + t_f$. Because of statistical nature of the t_s , the t_d is also a stochastic quantity with Laue distribution

$$\frac{n(t)}{N} = \exp\left(-\frac{t-t_f}{\langle t_s \rangle}\right),$$

where N is the total number of breakdowns, $n(t)$ is the number of breakdowns with $t_d > t$, $\langle t_s \rangle$ is the average value of t_s . The quantity $\langle t_s \rangle$ is the average reciprocal frequency of effective electron appearance Z , $\langle t_s \rangle = 1/Z$. So from the analysis of the $n(t)/N$ dependence it is possible to find the Z values. Fig. 1 depicts that for wide interval of photon flux F changing, the linear dependence between Z and F is observed. Coefficient γ has the meaning of quantum yield of electron emission.

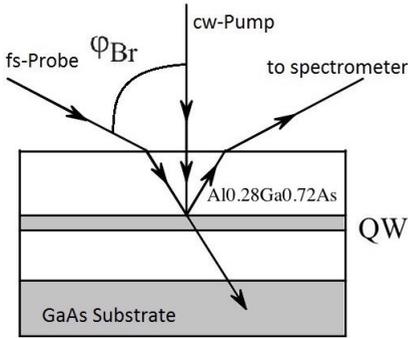
The results show that the illuminating discharge tube causes the emission of electrons in the anode region. Clearly, the photoionization of gas and the photoemission from the electrode surface are impossible for the wavelengths used for the illumination. As a possible mechanism, electron photo-desorption from the glass-wall surface facing the anode could be considered.

TPump-probe Reflection Spectroscopy of Excitons in Single GaAs/AlGaAs Quantum Well

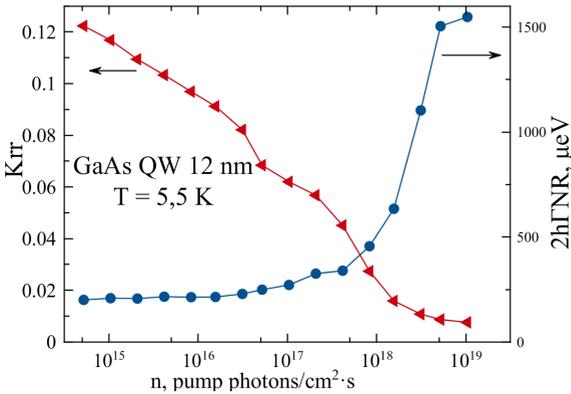
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GaAs/InGaAs/AlGaAs semiconductor structures with quantum wells are supposed to be the most promising for optical computer elements. They transform the intensity of received radiation nonlinearly, which is the necessary attribute for this purpose.



This work is devoted to the experimental measurement of the probe-radiation reflectivity dependency on the intensity of resonant monochromatic pump tuned to the light hole exciton of GaAs/AlGaAs epitaxial heterostructure E296 with 12 nm GaAs quantum well surrounded by $Al_{0.28}Ga_{0.72}As$ 66,2 nm barriers.



Experimental data indicate that the coefficient of resonant reflectance exponentially decreases with increasing pumping intensity. The inhomogeneous broadening of the spectral lines increases linearly, radiational width remains unchanged.

Exciton spectral line broadening due to the influence of scattering

mechanism of scattering in probe excitons on the particles formed in the semiconductor at high intensities pump.

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Manifestation of the Resonance Dipole-Dipole Interaction in IR Spectra of α -Crystalline C_2F_6 Thin Films in Spectral Regions of the ν_5 and ν_{10} Vibration Modes

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We studied the RAIR (reflection-absorption infrared spectroscopy) spectra of α -crystalline C_2F_6 thin films. Those films were obtained by deposition of gaseous C_2F_6 on a gold-plated copper mirror at the temperature, which varied between 10 and 80 K. The strong in absorbance bands ν_5 (band intensity $A(\nu_5)=290$ km/mole) and ν_{10} ($A(\nu_{10})=1010$ km/mole) [1] have complex contours. The shapes of these contours are explained by resonance dipole-dipole (RDD) interaction of the spectrally active equal molecules.

We interpreted complex contours of the ν_5 and ν_{10} bands considering two effects: Davydov splitting ($\Delta\nu$ (DS)) and LO-TO splitting ($\Delta\nu$ (LO-TO)). In our research, we found abnormally large band shift of asymmetrical isotopologue $^{13}C^{12}CF_6$ in crystalline spectrum compare to a band shift of a free molecule in the low-temperature solution spectrum. This abnormality was explained by intermolecular RDD interaction between asymmetrical isotopologue $^{13}C^{12}CF_6$ and surrounding main isotopologues $^{12}C_2F_6$.

Acknowledgements. This work was supported by the RFBR, 16-33-00040 mol_a. The spectroscopic measurements were performed on the apparatus of the Resource Center Geomodel of SPb State University.

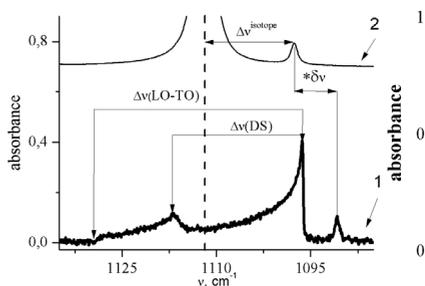


Fig.1: Spectral region ν_{10} band of the α -crystalline C_2F_6 film at temperature 70 K (spectrum 1) and low-temperature solution C_2F_6 in liquid N_2 at $T=77$ K [1] (spectrum 2). Arrows point at splitting $\Delta\nu$ (DS), $\Delta\nu$ (LO-TO), and isotopic band shift of isolated molecules $\Delta\nu^{isotope}$ and the band shift of asymmetrical isotopologue $\delta\nu_i$ at the transition spectra.*

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Parametric Nonadiabatic Excitation of Collective Resonances in a Dense resonant Extended Medium

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Mediums with strong light-matter coupling become more and more interesting in quantum-optics and photonics. Resonant interaction of coherent radiation with such matter goes with multiple exchange of excitation energy [1]. In the case in which resonant medium is embedded into an optical cavity this exchanges exhibits polariton modes and frequency of each cavity mode splits into two components. In this paper, I investigated specific features of the emerging coherent radiation in intracavity and free space regimes. Results of observation of the excitation of cooperative polariton resonances in rubidium vapor pumped by femtosecond (Ti:Sph) laser in free space are presented.

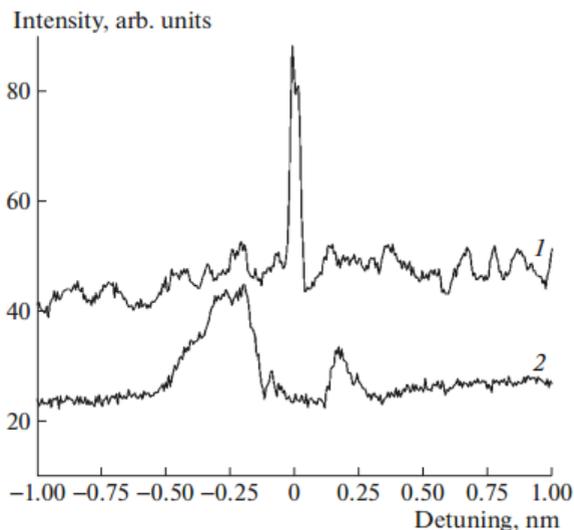


Fig. 1. Spectrum of superradiance of Rb vapors in the regimes of weak (1) and strong (2) coupling: (1) cell temperature 99°C, (2) cell temperature 161°C. Wavelength detuning is given relative to wavelength $\lambda = 794.7$ nm.

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Quantum-Mechanical Calculations of the Formaldehyde Dimer and its Complex with Hydrogen Fluoride

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Hydrogen bonded complexes of formaldehyde with hydrogen halides are of considerable interest from the experimental and theoretical points of view; however, they are insufficiently studied mainly due to the tendency of formaldehyde to self-association. For this reason, we first calculated the structure and spectroscopic properties of the formaldehyde homodimer $(\text{H}_2\text{CO})_2$ and then considered the 2:1 complex $(\text{H}_2\text{CO})_2 \dots \text{HF}$. The equilibrium geometries of the systems and the frequencies and intensities of vibrations in the harmonic approximation were determined using the Gaussian09 package of programs by the MP2/6-311++G(3df,3pd) method with the BSSE corrections. The anharmonic calculations were carried out using the approaches developed at the Department of Molecular Spectroscopy of St. Petersburg State University [1, 2]. Anharmonic values of vibrational frequencies and intensities were obtained by the variational method with potential energy surfaces calculated in the same approximation as the equilibrium structures.

The calculations predict a value of 13 kJ/mol for the binding energy of the homodimer, which is sufficient for the creation of noticeable concentration of these complexes. Upon their formation the C=O bonds become longer and weaker, and the strongest C=O band is red-shifted. The binding energy of HF with $(\text{H}_2\text{CO})_2$ in the $(\text{H}_2\text{CO})_2 \dots \text{HF}$ trimer was found to be 33 kJ/mol, which is slightly lower than the binding energies with other electron donors. The HF bond length becomes shorter by 0.017 Å upon complexation, the HF stretching frequency is lowered by about 400 cm^{-1} , and the HF intensity increases by a factor of 5. The most reliable spectral parameters necessary for experiments were derived from anharmonic calculations. For example, the anharmonic HF frequency value is lower by 200 cm^{-1} than the harmonic value.

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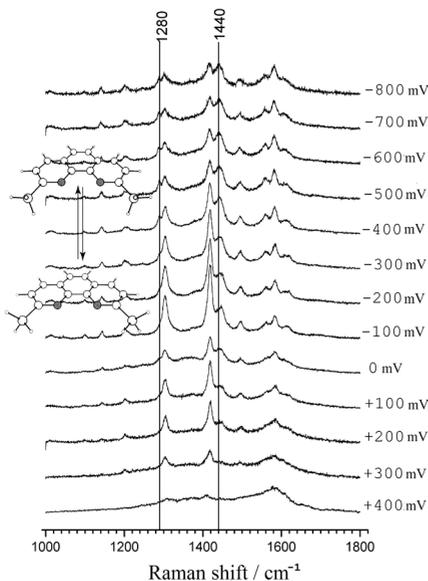
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SERS Study of Methyl Groups Rotation: 2,9-dimethyl-1,10-Phenanthroline Adsorbed on a Silver Electrode Surface

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Surface-enhanced Raman scattering (SERS) is a method widely used to study the properties of molecules adsorbed on metal surfaces. Because of adsorption of molecules Raman signal increases in 3-9 orders of magnitude in comparison with the molecule in volume. The great value of SERS spectra intensity makes this method as highly sensitive and non-destructive for detection of traces of various substances. For the development of quantitative analytical applications SERS requires additional study of the possibility of creating reproducible conditions of processing the metal surface and the sorption of an agent. SERS spectra from the surface of the silver electrode measured in a three-electrode electrochemical cell. The aim of this work was to study the conformational changes of 2,9-dimethyl-1,10-phenanthroline, adsorbed on a silver surface according to SERS. To do this it was necessary to study the maximum possible range of potentials of substrates. For surface stabilization, in particular for "conservation" of adatoms



commonly used solutions of halide anions. However, in the presence of halides the potential of silver dissolution decreases more than 300 mV compared to systems that do not contain halides, which makes the registration of SERS spectra of the adsorbate impossible at high positive potentials of the surface. Therefore, we worked out the experiment using a background electrolyte of KBF₄. The dependence of the spectra with the electrode potential evolution was shown in Fig. The range of potentials was determined in which there is a reversible conformational change: (-200 – -600) mV (relatively to saturated silver chloride electrode.). From these results we concluded that the conformational equilibrium related to the position of methyl groups defines SERS spectrum.

From these results we concluded that the conformational equilibrium related to the position of methyl groups defines SERS spectrum.

Influence of Active Electrode Shape on Streamers

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The aim of this experimental research is to test the following theory. There is the dependence of the average breakdown field strength on the parameter which characterizes the degree of the inhomogeneity of the electric field for simple electrode systems, such as sphere-sphere and sphere-plane. The experimental data of this dependence form Peak's curves.

The research of the streamers processes in the inhomogeneous electric fields for the electrodes with the complex geometry was performed. Installation scheme was as follows: the small cone acting as heterogeneity, was attached to the cylindrical electrode. A plane acts as a counter electrode. The distance between electrodes, the radius of curvature of the electrodes, the height and diameter of the cones are variable parameters. This system has been simulated in the program COMSOL Multiphysics. The simulation results and the experimental data were compared.

The universal curves for systems with complex geometries cannot be used for accurately calculating, but it can help to get a rough estimate. In other words, if the experiment wasn't conduct we cannot get close lines to the Pick's curves, because it is necessary to choose new characteristic diameter for each new geometry.

Precise Tuning of Fano Resonance in Hybrid Oligomers via Femtosecond Laser Melting of Plasmonic Nanoparticles

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Fano resonances in plasmonic and all-dielectric nanoparticle oligomers [1] offer a wide range of perspective applications for boosting nonlinear optical effects, bio-sensing, surface-enhanced Raman scattering, and potentially for quantum optics [2]. In terms of practical applications, it is necessary to have an approach for controlling the Fano resonances position in the oligomers. Recently developed asymmetric metal-dielectric (Au/Si) nanodimers allowed to tune their optical properties via femtosecond laser melting at nanoscale [3]. The hybrid nanodimer that includes a silicon (Si) truncated nanocone and a plasmonic (Au) nanodisc which is placed on the top of the nanocone. The Si nanocone is characterized with electric and magnetic dipole Mie-type resonances while the Au nanodisc has plasmonic resonance. It has been demonstrated that an important feature of such nanostructure is the possibility of modification of the Au nanodisc to a nanocup or even to a nanosphere via fs-laser irradiation of the nanodimer. Moreover, after fs-laser modification of Au nanoparticle the spectral position of its plasmonic resonance shifts to shorter wavelength region. It can be used for precise tuning of Fano resonance in oligomers composed of such hybrid nanodimers (see Fig. 1).

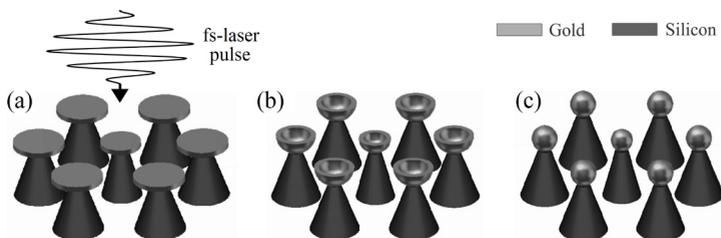


Fig. 1. Sketch of the oligomer structures composed of hybrid Au/Si nanodimers with different shapes of Au nanoparticles: (a) nanodiscs, (b) nanocups, and (c) nanospheres.

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Chiral Near-Field Formation with All-Dielectric Nanoantennas

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Nanophotonics has paved the way towards unprecedented level of an optical near-field manipulation at the nanoscale by means of plasmonic and rarer dielectric resonant nanostructures. This became possible after the emergence of optical antennas (or nanoantennas). Currently, nanoantennas have been used to control the local density of optical states, for single nanocrystal and molecule excitation, precise positioning at the nanoscale [1], controlling the scattering directivity, and for the efficient generation of higher optical harmonics [2]. Recently, study of nanoantennas for formation of chiral distributions of the near-field has gained considerable interest.

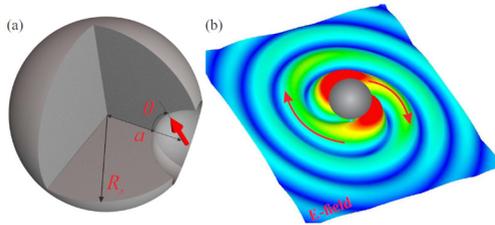


Fig. 1. (a) General view of the considered all-dielectric nanoantenna and orientation of the dipole source (red arrow). (b) The asymmetric arrangement of the dipole source provides the formation of chiral near-field emission.

Here, we study the asymmetric excitation of high-index dielectric subwavelength nanoantenna by a point source, located in the notch at the nanoantenna surface [3]. The nanoantenna (Fig. 1a) is a spherical nanoparticle made of a dielectric material with a high dielectric constant. We observe the generation of the chiral near-field distribution (Fig. 1b), which is similar to that of a circularly polarized or rotating dipole. Using numerical simulations, we show that this effect is the result of a higher multipole modes excitation within the nanoparticle. Further, we employ this effect for the unidirectional launching of guide modes in the dielectric and plasmonic waveguides. Our results are important for the integrated nanophotonics and quantum information processing systems.

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New Insights in Photosensitive Materials

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Here we report on light induced structuring and deformation of three photosensitive polymers differing in their glass transition temperature. To inscribe surface relief gratings, the polymer films were irradiated with interference pattern of different polarization: intensity interference pattern (IIP) and polarization interference pattern (PIP). The irradiation was conducted in-situ while simultaneously acquiring the topography change with AFM. The polymers show comparable kinetic of topography change and maximally attainable grating height under irradiation with IIP. The illumination with PIP results in larger grating height for all three polymers, but more pronounced topography change was found for the polymers of larger glass transition temperature.

We have also performed experiments where a rectangular piece of polymer film was cut out of the film using AFM lithography and irradiated with homogeneous light of linear polarization. For all three polymers we have found that the rectangular piece elongates along the electrical field vector and contracts in perpendicular direction.

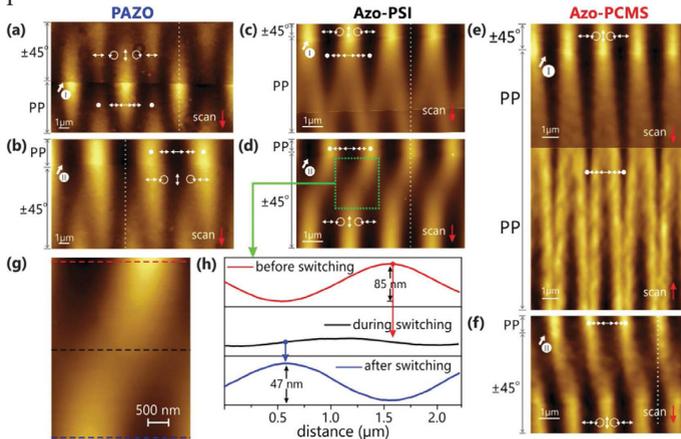


Fig. 1. [1] Switching experiments: comparison of SRG formation in PAZO (a, b), azo-Psi (c, d) and azo-PCMS (e, f) films using irradiation with $\pm 45^\circ$ and PP.

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Simulations of Glow-to-Arc Transition in Noble Gases

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Main types of direct current self-sustained discharges such as Townsend, glow and arc in microscale electrode geometries are objects of constant scientific interest. According to classic textbooks [1], each of discharges has its own section of the current-voltage characteristics (Fig. 1a). The main difference of arc discharge from Townsend and glow discharges is the mechanism of self-sustainment. Townsend and glow discharges with cold cathode are self-sustained by secondary electron emission caused by ions accelerating in cathode fall and bombarding cathode surface. Arc discharges are sustained by thermionic emission from cathode surface. At high pressures arc discharge can be self-sustained by ions accelerating in cathode fall and heating cathode surface.

The object of our study was glow-to-arc microdischarge transition, which still is not described in scientific literature despite the long history of discharge research. From a practical point of view, the interest results from, for instance, the possibility to use it in hollow cathode of stationary plasma thrusters.

In this work a model for simulation of direct current discharge in a wide range of currents was built to capture glow and arc discharges and transitions between them. Extended fluid model was coupled with gas heating equation for self-consistent simulation of discharge at atmospheric pressure in a wide range of currents. Both secondary electron emission and thermionic emission were taken into account simultaneously. In order to properly account for thermionic emission cathode heating was considered – heat flux equation was solved in a 1D solid domain with heat fluxes on cathode surface from discharge domain used as boundary conditions. Time-dependent simulations allowed for obtaining dynamics of discharge formation. Results of discharge simulations with different external parameters (gap, pressure, cathode type and geometry, gas, etc.) are presented. An example obtained by numerical simulation of current-voltage characteristics represented in the Fig. 1b.

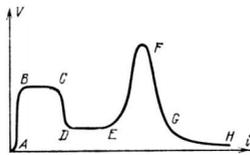


Fig. 1, a

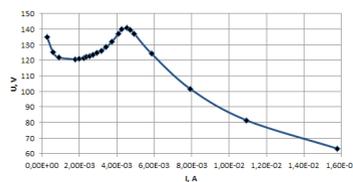


Fig. 1, b

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Modeling of Thickness Effect in NEXAFS C1s- Spectra of C₆₀

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The results of the thickness effect [1] modeling in the absorption cross section spectral dependences of the C₆₀-films with thickness d in the NEXAFS C1s-spectra are discussed in current work. The calculations were performed in Mathcad package using the ratio [2]:

$$\sigma(E) = -\frac{1}{n \cdot d} \cdot \ln \left[k \int e^{-\sigma'(E) \cdot nd} \cdot \varphi(E - E') dE' \right]$$

where n - concentration of absorbing atoms in the sample; k - normalization constant; σ and σ' - measured and true absorption cross section, respectively; $\varphi(E-E')$ - spectrometer apparatus function, which is selected as normalized to unity Lorenz function with half-width equal to 0.15 eV.

Measured by the TEY technique the absorption cross section are used as the original (undistorted) dependence $\sigma(E)$.

The calculation results are presented in Fig. 1. It can be seen that the peaks intensity is decreases with successively increasing film thickness. The modeling results are in good agreement with the cross section experimental data obtained by the transmission method.

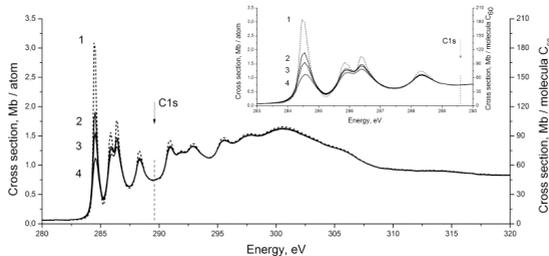


Fig. 1. Absorption cross section spectral dependences of C₆₀ in NEXAFS C1s-spectra, measured by TEY technique (true spectrum) (1) and calculated for different C₆₀-film thickness $d=60$ nm (2), $d=145$ nm (3) and $d=260$ nm (4).

Acknowledgements. This work was supported by the Grant of RFBR and Ministry of Economy of the Komi Republic № 16-42-110610 r-a.

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Modification of Polymer Particles in the Complex Plasma

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Nanoscale surface modifications of polymeric spherical particles occurring in complex dusty plasma have been investigated. Melamine-formaldehyde resin (MF-R) particles have been collected from a dust trap after levitation for various period of time. This experiment used the discharge chamber specially designed for trapping, collecting and extracting dust particles [1]. Decreasing in the average diameter of particles and changing in the surface morphology of particles were obtained. It is shown on Fig. 1. and Fig. 2. These changes were determined by electron microscopy techniques.

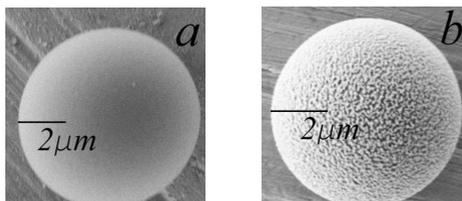


Fig. 1. Original particle MF-R (a) and particle after being in plasma (b).

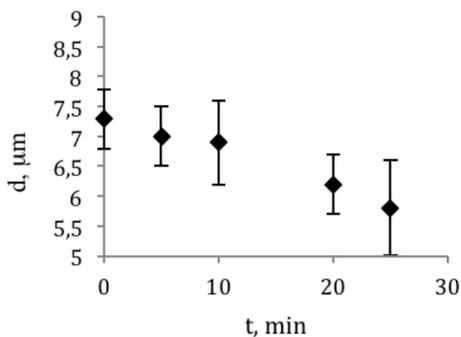


Fig. 2. Dependence of particle diameter from time spent in plasma.

Acknowledgements. This work was supported by the RSF (grant №14-1200094).

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Trajectories of Charged Particles in Dusty Plasmas

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Nowadays researches of dusty plasma develop rapidly [1]. One of current problems is to study ions and electrons trajectories in a self-consistent field of dust particle. It is believed, that test charge put in a plasma creates a disturbed region of the space charge layer, which can be described by screened Coulomb potential

$$U(r) = U_0 \frac{a}{r} * e^{-\left(\frac{r-a}{d}\right)}, \text{ where } a \text{ is particle radius, } d \sim \sqrt{\frac{kT_e}{4\pi n e^2}} - \text{screening}$$

parameter order of the Debye radius. If $d \gg a$, particles move in non-screened Coulomb potential. One or another case occurs depending on different discharge conditions. The trajectories of particles movement in a central field have the form

$$\phi(r, b, E) = \int_0^r \frac{\frac{b}{r'^2}}{\sqrt{1 - \frac{b^2}{r'^2} - \frac{U(r')}{E}}} dr' \quad [2],$$

where b is impact parameter.

Ions and electrons movement is considered under specific conditions:

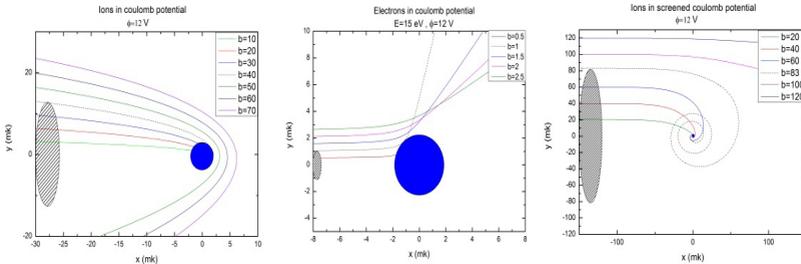


Fig. 1. The trajectories of ions and electrons movement and absorption cross section (dotted line).

While calculating ion current to the dust particle, limitation motion of ions should be taken into account.

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Infrared Study of RDD Interaction between Coadsorbed Molecules

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Spectra of adsorbed molecules, besides the data on surface sites, provide information about lateral interactions in the adsorbed layer between them. The dynamic or resonance dipole-dipole interaction (RDDI) can be distinguished from the static interaction by isotopic dilution. Up to now, RDDI has been studied between identical molecules, such as SF₆ [1] or CF₄ [2]. Here we show that RDDI occurs also between different molecules if their frequencies are close enough.

We have studied coadsorption of NF₃ with ³⁴SF₆ on ZnO. Both the molecules have extremely high absorbance and ³⁴SF₆ (1) or NF₃ (4), and after addition of NF₃ doses to ZnO with preadsorbed ³⁴SF₆ at 77K (2, 3).

NF₃ (905 cm⁻¹) is close to that of ν₃ vibration of ³⁴SF₆ (~915 cm⁻¹). As can be seen from the Fig 1, the spectrum of coadsorbed molecules cannot be presented as a combination of the spectra of the two species adsorbed separately. It is noticeable that on the high-frequency slope of this band an anomaly arises at about 900 cm⁻¹, which can be explained is a result of Fermi resonance between the vibrations of different molecules, ν₃ mode of NF₃ and ν₃ vibration of adsorbed ³⁴SF₆. Thus, the results obtained can be explained as a manifestation of strong RDD interaction between the molecules of two compounds. Computer modelling of the spectrum within the approach of isotropic oscillator pair interactions are in progress.

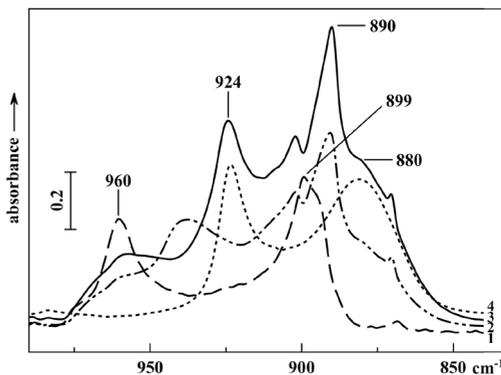


Fig. 1: FTIR spectrum of ZnO with adsorbed ³⁴SF₆ (1) or NF₃ (4), and after addition of NF₃ doses to ZnO with preadsorbed ³⁴SF₆ at 77K (2, 3).

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NEXAFS Study of Antarctic Ice Fishes Bones and Mineralized Formation

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Antarctic ice fishes habituate under extreme condition in deep, oxygen-poor, cold waters and due to specific adaptation can withstand temperature about $-1,9^{\circ}\text{C}$ that freeze the blood of all other types of fishes. In addition, they are characterized by some unique physiological adaptations like hemoglobinless (white) blood, large heart, low scales naked body, antifreeze protein presence, etc. The ice fishes differ from other vertebrates in respect of bone mineralization degree: their bone contain appreciably less mineral and have reduced density.

Bone is a composite material composed of organic (primarily collagen) and inorganic (bioapatite, $\text{Ca}_{10}(\text{PO}_4)_3(\text{OH})_2$) components, as well as lipids and water. Compared to collagen, the chemical and mechanical properties of the mineral phase of bone (bioapatite) are not well understood.

Current study include investigation of NEXAFS C1s-, N1s-, F1s-, P2p-, and Ca2p-spectra of bones and other mineralized formations isolated from the selected icefishes such as otoliths, scales, spines, fin rays and teeth as well as control Ca-based compounds and minerals. All NEXAFS-spectra were measured in total electron yield (TEY) mode at synchrotron source BESSY II using radiation from the Russian-German dipole beamline.

Acknowledgements. This work was supported by grants RFBR 16-32-00441mol-a and G-RISC P-2013b-19.

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Comparison of Electron Beam and Photolithography Methods

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Lithography is used for engraving microimages on a surface. Most lithographical methods are performed the following way: cleaning the surface, laying on the resist, exposure & development, etching, cleaning the surface. Each step has various experimental parameters to be chosen, such as selection of resist and fitting etching time.

The objective of this work was to fit parameters for photolithography and electron beam lithography, to perform them on substrates of different materials using different etching methods and to compare the results. 5 glass substrates were covered with photoresist and exposed with 1x1mm square pattern. Then the samples engaged HF-based buffer oxide etch during different periods of time. By measuring the depth of wells with an AFM, the etching speed was calculated. Then the desired pattern was exposed and etched to a depth of 100nm during ~20s. 5 Si substrates were processed the similar way: covered with PMMA (electron resist), exposed with the same pattern. These samples were etched with Ar plasma using Oxford Ionfab 300. Etching to the same depth took ~110s. All technological processes carried out on the facility of RC “Nanophotonics”.

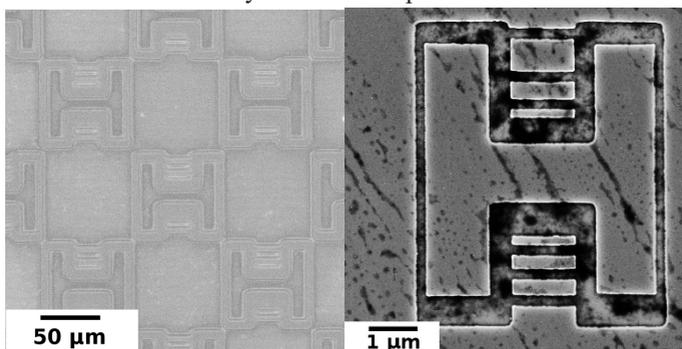


Fig. 1. – Patterns on glass substrate made with optical method, image from optical microscope (left) and on Si substrate with electron beam method, image from electron microscope (right).

Resolution of photolithography is significantly lower than of electron: minimal size of an element was 3.5μm vs 240nm. But the laser exposure rate is much higher than the electron beam: several minutes for few cm² vs several hours for few mm².

Automated Investigation Method of Polymer Solutions and Mesogen Melts Electrooptical Properties in Strong Electric Fields

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We present automated investigation method of electric birefringence (EB) which was successfully used for the research of polymer solutions and melts of isotropic phase of liquid crystals near the phase transition isotropic liquid - liquid crystal.

This method which enables us to measure both high and low EB values was used in the studies of free relaxation of birefringence in solutions of high molecular weight PBIC depending on the strength of applied polarizing electric field.

Changes in relaxation processes with increasing electric field were revealed. It was established that the average relaxation time decreases with increasing field [1].

The behavior of liquid crystals in the vicinity of temperature of the transition from the isotropic to nematic state was studied by the same method.

It was established that the electric field induces the isotropic—nematic phase transition in melts of these compounds. A relaxation process was discovered that destroys the nematic ordering induced in substances by electric fields. It was found that the relaxation time τ of the orientational order parameter is proportional to the square of electric field strength [2].

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Wireless Power Transfer System Based on Dielectric Resonators

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We propose a novel magnetic near field resonance wireless power transfer system based on high permittivity dielectric resonators. Magnetic dipole and magnetic quadrupole modes of the resonator are investigated as the operating modes of the WPT system. The maximal efficiency of 60% at magnetic dipole mode and 80% at magnetic quadrupole mode can be experimentally obtained. Further, the system operating at magnetic quadrupole mode is proved to be more stable to the mutual orientation of the transmitter and receiver.

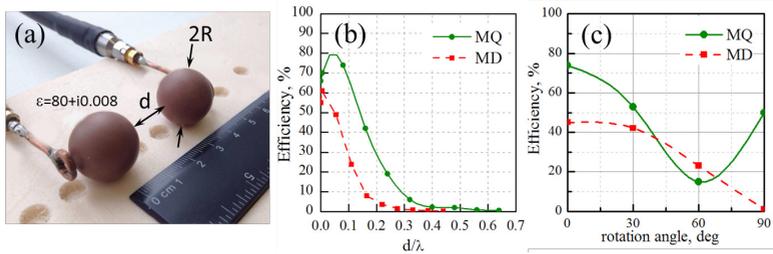


Fig. 1. Design of the WPT system based on high permittivity dielectric resonators of radius R separated by the distance d . Metallic loops are used to excite the transmitting resonator and to receive the energy from the receiving resonator. (b) WPT efficiency of the system operating at MD and MQ modes as a function of normalized distance.

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Destructive Mode Interference in TiO₂ Cylinders with Coaxial Void

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Nonradiating current configurations are very interesting for physicists and engineers for last decade as possible systems for effective cloaking and camouflage. Destructive mode interference is interesting for achievement suppression of far-field scattering; it can lead us to non-radiating sources. Toroidal and dipole moment irradiations can destructively interfere with total suppression of far-field radiation [1, 2].

Here we demonstrate numerically that TiO₂ microparticles can exhibit destructive mode interference in the range 1-3 THz. In this work we are using TiO₂ particles which have extremely high dielectric permittivity $\epsilon \approx 100$. We achieve the spectral overlapping of the toroidal and electric dipole modes through geometry tuning and observe a highly pronounced dip in the far-field scattering. We also achieve toroidal and electric dipole modes overlapping at the resonant frequency with total suppressing of total electric dipole moment.

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Investigation of the Parameters of Microplasma Detectors PLES in Helium Using Diagnostic Scheme Plasma Probe Analyzer

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Researches to develop methods for the analysis of gases have a great practical meaning. There are many different gas analysis means. In particular, there are methods of mass spectrometry and gas chromatography. However, their disadvantage are the requirement of high vacuum in the detector, and the cost of considerable size. The most effective and well-known methods of analysis substances are electron spectroscopy methods. They are based on the definition of the characteristic electron energy E_e and particles B^* with fixed energy E_p (photons excited atoms, etc.), the measurement of which allows us to analyze the atomic and molecular structure. The composition and structure of various samples (see. e.g., [1])

$$A+B^* \Rightarrow A^+ + B + e(E_p). \quad (1)$$

According to the measured energy E_e (electron spectrum) and known energy E_p of particles B^* is the ionization potential E_i atoms or molecules of the desired A , $E_i = E_p - E_e$ and thus, it is determined species A .

As noted in working [1] environment microplasma detectors should be used nonlocal plasma afterglow or negative glow plasma glow discharge. In this case, the temperature of the core group of electrons is a few tenths of eV. In this paper, to study the parameters of microplasma detector circuit used Plasma Probe Analyzer [3], allowing us to obtain the function of the electron energy distribution. The buffer gas of experimental microplasma detector was helium and different portions of the atmospheric air. Fig. 1 shows the CVC, its first and second derivative and EEDF for helium – air (1%) mixture obtained by Plasma Probe Analyzer.

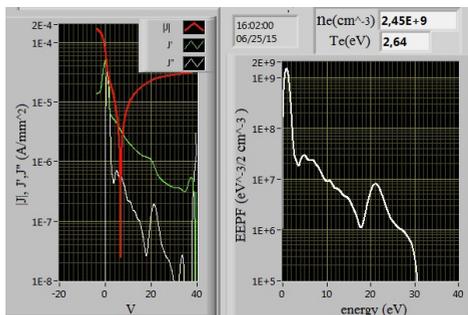


Fig. 1. Current-voltage characteristic and EEDF in mixture He+Air (1%), pressure 6 Torr, current 7mA.

The buffer gas of experimental microplasma detector was helium and different portions of the atmospheric air. Fig. 1 shows the CVC, its first and second derivative and EEDF for helium – air (1%) mixture obtained by Plasma Probe Analyzer.

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Resonant Optical Heating of Silicon Nanoparticles

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Recently there has been growing interest in thermo-plasmonics. Plasmonic (metallic) nanoparticles can be used as nanoscale heat sources, due to their ability to resonantly absorb incident light and effectively increase local temperature. These nanoparticles are already being used in cancer treatment, drugs delivery, nano-chemistry and optics [1]. However, metallic nanoparticles do not possess either fluorescent or Raman response, which are frequently used for nanoscale thermometry. Therefore, it remains unclear how to control the local heating by means of plasmonic nanoparticles. In turn, dielectric nanoparticles possess own Raman signal [2], which is very sensitive to temperature.

We propose a new type of heat nanosources – resonant silicon nanoparticles. On the one hand, low-optical losses allow for excitation of high-Q Mie-resonance. On the other hand, even small imaginary part of silicon dielectric permittivity results in strong heating. We experimentally demonstrate controllable temperature variation of silicon nanoparticles under their laser irradiation. We reveal that the excitation of magnetic modes yields significantly much more effective conversion of incident light to heat as compared to electric ones. In particular, we achieve temperature increase up to 900°C at magnetic octupole with a 633-nm laser intensity of 2mW/μm². The experimental results are in good agreement with developed analytical and numerical models of resonant nanoparticles optical heating. Our results pave the way to sub-diffractive optical heating with simultaneous highly sensitive nano-thermometry.

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G. Theoretical, Mathematical and Computational Physics

Correlation Coefficients in the Model with String Fusion on Transverse Lattice

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The multiple hadron production in high energy collisions is studied in the framework of the simple model which enables to take into account the effects of a color quark-gluon string fusion [1, 2]. The model with a lattice in transverse plain is used for the calculation of the correlation coefficients between multiplicities and between the average transverse momentum and the multiplicity in realistic case of non-uniform string distribution in transverse plane. The asymptotes of the correlation coefficients at large string density are found. It is shown that the received asymptotes in case of uniform string distribution in transverse plane are transformed into the ones obtained in papers [2-4].

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Influence of Ion-Dipole Interactions between Polyaspartatic Acid and Calcium Ions on Organo-Mineral Complex Formation

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Polymers, which contain groups that are capable of ionization, are often used as scale inhibitors due to the ability of chelating mineral ions from solution forming organo-mineral complexes. Polyaspartatic acid, which contains carboxyl groups, is biodegradable, water soluble, biocompatible. Due to these properties, polyaspartatic acid is preferable for wastewater treatment applications [1]. Since polyaspartatic acid is ionized in an aqueous environment, formation of organo-mineral complex occurs as a result of ion-ion interactions between carboxyl groups and cations. However, influence of ion-dipole interactions of amid and non-ionized carboxyl groups of polyaspartatic acid with salt ions on the formation of organo-mineral complexes still remains unexplored.

To study this influence the atomistic molecular dynamics simulations of neutral polyaspartatic acid molecule in calcium chloride aqueous solutions at different concentrations were carried out. Comparison of the polymer active group interactions with calcium ions, water molecules and with each other has been done. As well as the average lifetime of contacts of calcium ions with carboxyl groups was calculated. It was observed that ion-dipole interactions do not lead to the formation of stable organo-mineral complex.

Acknowledgements. Work performed using supercomputer system NRC "Kurchatov Institute" resources.

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Primary and Secondary Vertices Reconstruction in the BM@N Experiment

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This report discusses the issue of the vertex finding at BM@N experiment, which aims at studying collisions of the elementary particles and ions with a fixed target at energies (laboratory system) up to 4 GeV per nucleon (for Au79+) [1]. To find the vertices, different methods have been developed.

For the primary vertex finding, tracks, which were near to the target, were approximated by straight lines. Also it was the analysis of efficiency of the primary vertex finding realized. For the secondary vertices, tracks were approximated in pairs by splines or polynomials near to point of the closest approach. After the calculation of minimum distance between two tracks, some of the couples, which answered the criteria, were put to the Armenteros-Podolanski plane [2].

As a result, primary and secondary vertices were found and identification of Λ -hyperons and their decay products was done.

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Molecular Dynamics Simulation Study of Polylactide and Polyhydroxybutyrate

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Polymers derived from renewable resources have attracted an increasing attention in recent years. The application of such materials in different fields including medicine and food packaging, may decrease the environmental concerns caused by petroleum-based polymers, which penetrate into the ecosystem as industrial waste. The polylactide or polylactic acid (PLA) and polyhydroxybutyrate (PHB) are considered to be among the most promising biodegradable polyesters. Their thermal and mechanical properties allows using them as potential replacements of polymers synthesized from petroleum products [1,2].

The present work is devoted to the theoretical study of PLA- and PHB-based systems. The all-atom molecular dynamics simulations of bulk samples were performed using the Gromacs package [3, 4]. The cooling procedures for each system were carried out during the simulation. Temperatures of the glass transition (T_g) of PLA and PHB were calculated from the density dependencies for each system. It was found, that the GAFF force field can reliably reproduce the experimental difference of T_g between considered polymers, which is 51 - 68 degrees [1, 2]. Thus, developed and verified models of bulk samples can be used for the detailed atomistic investigation of PLA and PHB, and also blends and composites based on them.

Acknowledgements. This study has been supported by the Russian Science Foundation (State Agreement № 16-13-10485).

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Investigation of Relaxation Processes of Thermoplastic Polyimides

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Dielectric spectroscopy is one of widely-used experimental approach to investigate dynamics properties of thermostable polyimides (PIs). The dielectric properties of the individual PI were well studied experimentally, but relationship between dielectric properties and chemical structure of PIs remains unclear.

Computer simulations and experimental study of dielectric properties of PI R-BAPS based on 1,3-bis(3',4'-dicarboxyphenoxy)benzene (dianhydride R) and 4,4'-bis(4''-aminophenoxy)diphenyl sulfone (diamine BAPS) have been carried out in the present study. Full-atomic microsecond molecular dynamics simulations of PI R-BAPS have been performed using Gromacs package. The autocorrelation function for different vectors of the polymer chain has been calculated.

The dynamic properties of different dipole moments directed parallel and perpendicular to the polymer chain backbone have been investigated. The heterogeneous dynamics of dipole moments were observed.

Acknowledgements. This study has been supported by the Russian Ministry of Education and Science within State Contract No. 14.Z50.31.0002 (megagrant). The simulations have been carried out using the computational resources of the Institute of Macromolecular Compounds, Russian Academy of Sciences, the Chebyshev and Lomonosov supercomputers at Moscow State University, and computational resources of MCC NRC “Kurchatov Institute”.

The Rainbow Tables to Invert Cryptographic Hash Functions

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In the modern world there is the rapid development of information and computational technologies. The problem of data protection during storage and transmission of information becomes actual. In recent years the power of computational technology has increased dramatically, allowing us to develop sophisticated encryption algorithms.

Knowing the methods of hacking and attacks on the stored and transmitted data, it becomes possible to secure the information. Suffice it to encrypt the available data, and even the availability of comprehensive data does not guarantee the success of the attack. To store the password database is convenient to use hashing algorithms, as for any length of input values they produce a fixed-length string. There exist many hashing algorithms. As well as several known algorithms to recover one of the options available for the original data hash value. However, most algorithms have a huge time and capacity complexity. The best known method to find the inverse value of the hash function is the rainbow tables algorithm (Fig. 1) which uses a compromise approach "time-memory trade off" [1].

In this work there have been studied existing hash algorithms. A special attention has been paid to the «time-memory trade off» principle. The basic ways of cracking hash functions has been studied, including rainbow tables. For practical verification of hacking features two rainbow tables were generated for MD5 and SHA-1 encryption algorithms using RainbowCrack program [2]. Their performance has been analyzed.

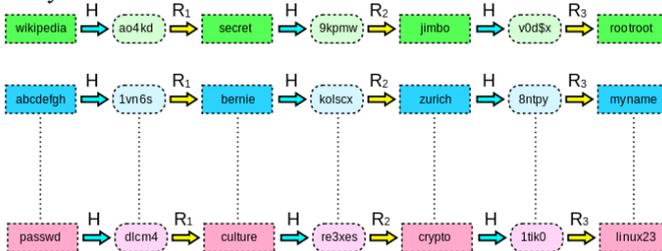


Fig.1 Scheme of simplified rainbow table.

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Confinement and Abrikosov Strings

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In spite of the fact that supersymmetry is still not found in the real-world experiments (such as those which are conducted at the LHC), it is not completely useless to study such theories. Supersymmetric extension of a usual theory may turn out to be simpler and even solvable, even though the initial theory was not. In this way one can obtain and study a model which can provide some qualitative results and insights in the physics of the theory one is interested in.

A nice example of such machinery at work is supersymmetric quantum chromodynamics (SQCD). Ordinary QCD is believed to describe strong interactions, that is, the physics of quarks and gluons. And although all high-energy experimental data are in perfect agreement with the calculations, there is still a problem with more or less direct verification in the low energy range. Here we will be talking mostly about confinement.

Simplifying the subject, confinement phenomenon can be described as quarks always holding together in groups with zero total color charge. In attempt to part them from one another one would end up only with more groups of quarks, and no free quark ever emerges. Present day situation is such that no one yet succeeded in obtaining strict explanation of this phenomenon from microscopic quantum chromodynamics. And we believe that here SQCD may come in handy.

The model under consideration is $SU(N) \times U(1)$ $N = 2$ supersymmetric QCD. In this model the gauge group gets broken in a special way, resulting in formation of vortices which carry non-Abelian fluxes and confind monopoles. They are called non-Abelian strings and are analogous to ordinary electrodynamics Abrikosov strings connecting in pairs monopoles and antimonopoles in superconductor.

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Specifics of Renormalization for the Quantum Yang – Mills Theory in the Four Dimensional Space – Time

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This paper describes the project of the renormalization, which uses the remarkable properties of the theory of Yang – Mills, such as asymptotic freedom, dimensional transmutation, and the distribution of singularity in the decomposition of actions in a series. As the main object we use the functionality of the external field or effective action. The formalism of the background field is well developed, we use it in the formulation where it is interpreted as the generating functional for S-matrix. We rely on the regularization based on the introduction of the cut-off momentum. This procedure is still not developed in full form, so we called our offer with scenario. We can introduce the classical action of the theory of Yang – Mills and decomposition for the effective action

$$S(A) = \frac{1}{4g^2} \int tr F \wedge F^* \quad W = \frac{1}{\alpha} W_{-1}(B) + \sum_{k=0} \alpha^k W_k(B).$$

After renormalization we have

$$W_{reg}(B, \alpha(\Lambda), \Lambda) = \frac{1}{\alpha_r(\mu)} W_{-1} + W_{0,0} + \sum_{n \geq 1} \alpha_r^n(\mu) W_{n,0},$$

where the coefficients do not have divergences and

$$\alpha_r(\mu) = e^{-L\beta(\alpha)\frac{\sigma}{\partial\alpha}} \alpha(\Lambda).$$

The new coupling constant satisfies the equation

$$\mu \frac{d\alpha_r(\mu)}{d\mu} = \beta(\alpha(\mu)),$$

total contribution at higher degrees is equal to

$$\frac{1}{\alpha_r} = \frac{1}{\alpha} + \beta_1 L + \frac{\beta_2}{\beta_1} \ln L.$$

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MD Modeling of Disulfide Bond Formation in Peptides and Proteins

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We are now at the dawn of the new era in protein modeling when it becomes possible to fold proteins in silico "from the first principles", i.e. using unbiased MD simulations. We have developed an empirical protocol to include the process of disulfide bonding into conventional (unrestrained) MD models of protein folding. The protocol has been tested on 15-amino-acid peptide guanylin, containing four cysteine residues. The fifty guanylin trajectories recorded with GPU-enabled Amber 14 program under ff14SB force field produced 45 disulfide-bonded folds, with the isomer distribution that is broadly similar to the one observed experimentally. The PBSA/GBSA energy calculations performed on these MD models suggest that the isomer distribution is under kinetic rather than thermodynamic control. We have also used the new protocol to simulate disulfide bonding in the terminal guanylin segment within the 94-amino-acid prohormone proguanylin. It is envisaged that in future an efficient reactive force field can be constructed along these lines to model protein oxidative folding.

Acknowledgements. This work has been supported by RSF grant 15-14-20038.

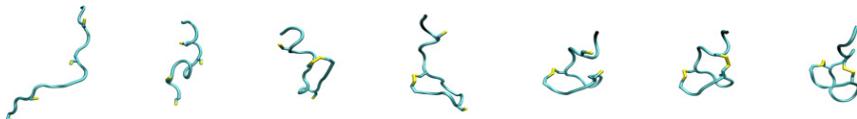


Fig 1: The process of disulfide bonds formation in guanylin. Snapshots are taken from MD simulation.

Description of Gravity in the Model with Independent Nonsymmetric Connection

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The current description of gravitation in modern physics is General relativity by Albert Einstein. It is providing a unified description of gravity as a geometric property of spacetime.

This work presents a generalization of General relativity. We consider the standard Einstein-Hilbert action in which the metric and the connection are considered independent variables. Therefore, the connection is not the Levi-Civita connection. Also we assumed a presence of torsion, i.e. $\Gamma_{\mu\nu}^{\alpha} - \Gamma_{\nu\mu}^{\alpha} = S_{\mu\nu}^{\alpha} \neq 0$. To obtain the equations of motion, one now has to vary the metric and the connection independently. As a result of variation, the metric equation of motion is nothing but Einstein equation. The connection equation gives us a arbitrariness in the determination of connection, i.e. presence of gauge invariance.

Then we entered a matter in the form of point particle which interacts with field of connection. Thus we added extra terms into the action. Also we complement action by a kinetic term for field of connection to the correct equations of motion. Thus, after the variation procedures, we obtain the Einstein equation, geodesic equation and Maxwell's equations for electromagnetism.

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Functional Determinant beyond the One-Loop Approximation

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The functional determinant and the heat kernel method has been proven to be an extremely valuable tool in many areas of mathematics and physics [1,2] especially for the study of the one-loop effective action in quantum field theory [3,4] and the vacuum energy. Nevertheless the determinant technique works well only in one-loop approximation. In this article we would like to calculate the two loops divergences using the standard trick with generating functional. This allows us to calculate two loops using the same method for a wide type of Lagrangian.

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Statistical Restoration of Broken Symmetry in Fully Developed Turbulence

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The fully developed turbulence remains a very important problem of theoretical physics. Although a great progress was achieved during the second half of the 20th century, the theory of turbulence still contains both elements of the analytical study and more phenomenological approaches. One of the main concepts of the phenomenological approach to the fully developed turbulence is the idea of the statistical symmetry restoration. The symmetries of the Navier-Stokes equation for fluid (isotropy, Galilean symmetry, time-shift invariance) are violated either by the initial and boundary conditions or spontaneously, as the Reynolds number increases. It is shown that in the incompressible case the isotropy restores for the equal-time structure functions in the inertial momentum interval.

Two-Particle Correlations Arising in Decay of a Single String

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The azimuthal dependence of two-particle correlations is analysed in the framework of the standard approach to string decay [1, 2]. In accordance with the Schwinger's mechanism [3] it is supposed that the decay of a string into segments take place due to a creation of quark-antiquark pairs in strong string color field. The string segments then evolve into observed hadrons. It is shown that the conservation of the transverse momentum of the produced quark-antiquark pair leads to the azimuthal correlations between particles produced from nearby string segments [4, 5]. In contrast with [5] we argue that this mechanism gives rise to the correlations in rather wide range of rapidity (up to a few units), contributing along with other possible mechanisms to the appearance of the so-called backward ridge-like structure in two-particle correlation function [4]. To explain the forward peak in the correlation function one has to take into account additionally to this mechanism the details of a string segment fragmentation into hadrons.

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Rare Annihilation Semileptonic B -Meson Decays

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Physics of B -mesons is still one of the active research topics both theoretically and experimentally. From experimental side, there is a very intensive study of B -physics mainly under the research plan by the LHCb collaboration at the LHC collider. After the B -meson factory Belle-II in KEK starts its physical run soon, the results obtained can be checked and extended by processes which are unobservable at the LHC. Both at the LHC and Belle-II, statistics collected is enough to make a detail study of rare semileptonic B -meson decays with the light π^- , K^- , K^{*-} , ρ^- , ω^- and φ -mesons in the final state like $B \rightarrow K^{(*)} \ell^+ \ell^-$, where $\ell = e, \mu$. At the moment, the smallest measured branching fraction of such decays is $Br(B^+ \rightarrow \pi^+ \mu^+ \mu^-) = (1.83 \pm 0.24 \pm 0.05) \times 10^{-8}$ [1]. The differential branching fraction in nine bins of the dilepton invariant mass squared, q^2 , and direct CP-asymmetry are also presented and compared with the SM predictions, being in agreement. Note that this process is rather sensitive to the contributions from the annihilation-type diagrams. There exist also semileptonic decays which are predominantly determined by the annihilation-type diagrams like $B^0 \rightarrow \varphi \ell^+ \ell^-$. The rare semileptonic B -meson decay $B^0 \rightarrow \varphi \ell^+ \ell^-$ is considered. Its partial decay rate is calculated in the interval [1 GeV², 8 GeV²] of the lepton-pair invariant mass squared and the 10% uncertainty connected with the choice of the B -meson distribution amplitudes' model (their shapes are taken from [2-5]) is explicitly demonstrated. The perturbative contribution to the total decay width only is estimated to be $Br \sim 10^{-12}$, so this decay can be, in principle, observed after several years of the LHC running.

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Critical Behavior of $U(n)$ - χ^4 -Model with Antisymmetric Tensor Order Parameter Coupled with Magnetic Field

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Investigation of critical behavior of Fermi particle systems is permanently in focus of attention due to the problem of superconductive phase transition. The nature and properties of this phase transition was an open question for decades. There are two main approaches to the investigation of this problem. First one is based on microscopic description of quantum gas, and allows to perturbatively reveal phenomenon of superconductivity. Second one can be applied to the description of a small neighborhood of transition point and is based on Ginzburg–Landau effective Lagrangian studied by means of field theoretic renormalization group. Because mean field theory can not be constructed in terms of Grassmann variables, the problem is to trace the connection between this two approaches. That connection has been traced in the work [1], where the authors have shown that critical modes of the simple microscopic model of fermions with n possible spin projections and density-density interaction can be expressed in terms of antisymmetric tensor fields, whose means appears to be an order parameter. It was shown that in the vicinity of phase transition point the behavior of such system can be described by ϕ^4 -like theory, with two independent interaction terms. This model was studied by the means of field theoretic renormalization group up to five-loops accuracy [2, 3].

In this work the critical behavior of $U(n)$ - χ^4 -model with antisymmetric tensor order parameter at charged regime is studied by means of the field theoretic renormalization group at the leading order of ε -expansion (one-loop approximation). It is shown that RG equations have no infrared attractive charged fixed points. It is also shown that anomalous dimension of the order parameter in charged regime appears to be gauge dependent.

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Substrate Influence on the Scattering Properties of Metal Nanoparticles Accounting for the Non-local Effect

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Interaction of light with plasmonic metallic nanostructures or nanoparticles is of increasing interest in various current research areas. The reason behind it is that plasmonics allows to manipulate light at the nanoscale and to obtain strong and very confined electromagnetic fields. The encountered effects are useful in such areas of science and technology as sensing, near-field optical microscopy, surface-enhanced raman-spectroscopy, nanoparticle lithography, light harvesting, and others [1].

Using these field enhancements to design specific nanoscale photonic systems requires a detailed knowledge about the occurring fields. One of the most significant problems appears to be the non-local interaction nature of the plasmonic medium which requires going beyond classical electrodynamics to describe occurring effects [1-4]. So it is necessary to have an advanced computer technology, which allows accounting for all features of interaction in the plasmonic structures down to Ångstrom dimensions and enables to provide reliable and accurate simulation results [5].

This presentation is focused on the development of an advanced mathematical model, which incorporates Non-Local Effect theories [1] into the efficient Discrete Sources Method (DSM) hybrid scheme [6]. It therefore enables to extend the range of DSM validity to a wide variety of plasmonic structures. Currently the new model is implemented for spherical particles and verified by comparing the results to the analytical solution available in [1].

In applications plasmonic nanoparticles usually have to be considered in a layered medium, i.e. deposited on a substrate that could drastically influence their scattering properties [4]. For this reason the developed model also includes the analytical account for substrate-particle interaction, which allows to rigorously investigate the substrate influence on particle's scattering properties.

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Vibration of a Droplet in Alternating Electric Field

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Both temperature and humidity can negatively affect the lifetime of the isolation of high-voltage equipment. Isolation can be affected by external conditions such as weather, temperature, sun rays and air humidity and by internal conditions such as condensed humidity. The vibration of a droplet under an alternating electric field causes the formation of an electric charge which in its turn leads to leaps in voltage in big shape deformations.

Our goal is to simulate the vibration of a droplet, determine the most dangerous combination of volume and frequency, analyze the ratio of eigenmodes and forced modes and to find the characterized radius at the resonance.

A water droplet in alternating electric field changes drastically its shape expanding and shrinking. Vibration at resonance of a water droplet was investigated. From the simulation of the droplet under electric field, the degree of deformation of its shape was evaluated by deformation rate. Under the relatively low AC electric field, a droplet vibrates more or less depending on the frequency of the electric field. It vibrates strongly at a particular resonant frequency. Depending on the frequency of the electric field and its size, the deformation ratio at shrinkage and extension changes significantly.

The height of the droplet under AC electric field varies from 1.2 to 1.5 times the height of the original droplet during vibration. The amplitude of eigenmodes and forced modes of the droplet are comparable for small values of its volume. Relative amplitude of deformation increases with the increase of the droplet radius. The ratio of surface tension to the Coulomb force decreases with the increase of the radius. The electric field might be causing the turbulent flow inside the droplet.

Homogenization of Elliptic and Parabolic Dirichlet Problems in a Bounded Domain

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The talk is devoted to homogenization of periodic differential operators. Let Ω be a bounded domain in \mathbf{R}^d with the boundary of class C^2 . We consider selfadjoint matrix differential operators $B_{D,\varepsilon}$, $0 < \varepsilon \leq 1$, acting in $L_2(\Omega; \mathbf{C}^n)$ with the Dirichlet boundary condition. The coefficients of $B_{D,\varepsilon}$ are assumed to be periodic with respect to some lattice in \mathbf{R}^d . The principal part of $B_{D,\varepsilon}$ is given in a factorized form; the lower order terms belong to suitable L_p spaces on the cell of periodicity. The coefficients depend on \mathbf{x}/ε and oscillate rapidly as $\varepsilon \rightarrow 0$.

Assume $B_{D,\varepsilon} > 0$. Let Q^ε be the operator of multiplication by a matrix-valued function $Q(\mathbf{x}/\varepsilon)$ that is bounded together with the inverse. For the generalized resolvent $(B_{D,\varepsilon} - \zeta Q^\varepsilon)^{-1}$ we obtain approximations in $(L_2 \rightarrow L_2)$ - and $(L_2 \rightarrow H^1)$ -operator norms with two-parametric (with respect to ε and ζ) error estimates. For a fixed ζ , the estimate in $(L_2 \rightarrow L_2)$ -norm is of the precise order $O(\varepsilon)$. The order of the $(L_2 \rightarrow H^1)$ -estimate is $O(\varepsilon^{1/2})$. It becomes worse because of the boundary influence. The results of such type are called operator error estimates in homogenization theory.

The proof is based on the continuation to the whole space \mathbf{R}^d , introduction of the boundary-layer correction term and homogenization results [1] for the elliptic operators acting in \mathbf{R}^d .

We also study the behavior of the semigroup $\exp(-B_{D,\varepsilon} t)$, $t > 0$. The method is borrowed from [2]. It is based on the integral representation for the semigroup due to the inverse Laplace transform. So, we can obtain $(L_2 \rightarrow L_2)$ - and $(L_2 \rightarrow H^1)$ -approximations for $\exp(-B_{D,\varepsilon} t)$ by integrating the corresponding two-parametric error estimates for the resolvent over a suitable contour in the complex plane.

We apply operator error estimates to homogenization of solutions of elliptic and parabolic problems.

The results are obtained jointly with Prof. Dr. T.A. Suslina.

Acknowledgements. The research is supported by the Chebyshev Laboratory, by JSC “Gazprom Neft” and by the “Dynasty” foundation.

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Normal Casimir Forces for 2d Gratings

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The Casimir effect is a quantum effect caused by vacuum fluctuations. If we consider two bodies separated by the vacuum this effect appears in the interaction of the bodies. Effect was discovered in 1948 by H.B.G. Casimir [1] and later it was supported by experiment. Nowadays a lot of different systems are considered under this problem.

This work is the generalization of the case of two bodies with periodical boundaries in one direction and translationally invariant boundaries in orthogonal direction [2].

Now we consider two bodies separated by vacuum with boundaries, periodical in two orthogonal directions. Theoretical formalism is performed for arbitrary materials and figures of the boundaries of the bodies. We use scattering theory, precisely Rayleigh decompositions [3] to calculate the Casimir energy.

We computed normal Casimir forces for the bodies of Silicon with sinusoidal geometries (Fig. 1) and compared the results with the force between two flats of Silicon.

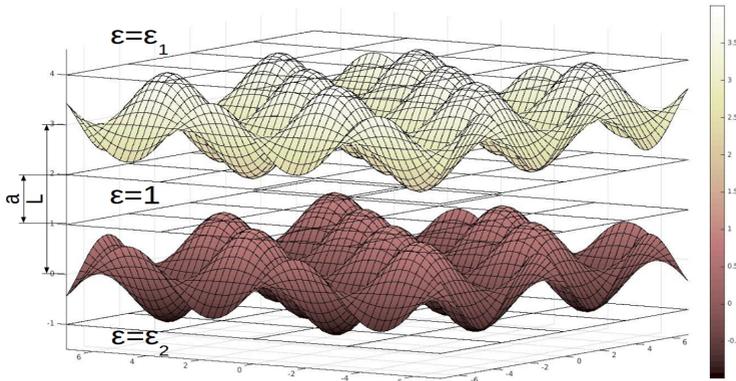


Fig. 1. Two media with sinusoidal geometry.

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The Influence of Flexoelectric Effect on the Fréedericksz Transition in Twisted Nematic

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Flexoelectricity is a property of some materials (e.g. nematic liquid crystals with polar molecules) to perform polarization induced by a strain gradient. In this work we introduced flexoelectric term into the free energy of twisted nematic and studied how the magnitude of the averaged flexoelectric coefficient \bar{e}_{13} influences electric field-induced Fréedericksz transition in twisted nematic cell. It turns out that Fréedericksz transition can be either continuous or discontinuous depending on \bar{e}_{13} . Another important issue is that the voltage of the Fréedericksz transition is less for materials with greater \bar{e}_{13} , providing all the other material constants are the same. This effect may be used to reduce the power consumed by different twisted nematic devices.

Calculations of Probabilities of Electron-Positron Pair Creation in Collisions of Highly Charged Ions

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It is well known [1-3] that energy levels of an atom dive into the negative continuum, given that the atom has sufficiently large charge of nucleus. The critical value of charge number at which 1s state reaches negative continuum is $Z_c \approx 173$. If the diving into the negative continuum level was initially unoccupied then it turns into resonance that can decay via creation of an electron in this energy level and emission of a positron. Unfortunately, atoms with such a large charge number do not exist. Yet it was shown [2, 3] that the same mechanism of pair creation one can see in the process of collision of ions with overall charge $Z \geq Z_c$. This mechanism is referred to as spontaneous pair creation, in order to distinguish it from dynamical pair creation that occurs independently of overall charge of colliding ions. Thereby low energy ion collisions provide physicists with a unique tool for investigation of quantum electrodynamics effects in presence of supercritical electromagnetic field.

Up to date the most of nonperturbative calculations of probabilities of electron-positron pair creation are confined within the monopole approximation [4-6] in which only spherically symmetric part of two center potential is taken into account. In this work nonperturbative calculations of probabilities of electron-positron pair creation were performed beyond the frame of monopole approximation. The calculation method is based on numerical solution of time-dependent Dirac equation in the basis of eigenfunctions of static one-center hamiltonian. These eigenfunction were obtained by using the dual kinetic balance method [7] with B-splines as basis functions.

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Experimental Verification of the Modified Phase Function Method for Calculating the Electrocoalescence Processes in Electrical Dehydrators

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An experimental mock-up was designed and implemented, which allows investigating the processes of electrodeformation and electrocoalescence (Fig. 1) of conductive droplets suspended in a non-conducting dispersion fluid. A set of experimental data has been obtained, which indicates all the necessary properties of fluids and the parameters of the experiment. A computer model has been implemented, which is meant for calculation of proposed processes in electrical dehydrators and is based on the modified phase function method [1]. The model has been verified on the basis of the dependences of the drop deformation degree on the drop radius and the voltage and its accuracy has been estimated.



Fig. 1. The coalescence of water drops in an electric field.

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Semi-Inclusive Eta- and Eta-prime Meson Production in Bottomonium Decays

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After the discovery of the first resonance, $Y(1S)$ -meson, from the family of the bottomonium in 1978, experimental data on the bottomonium spectroscopy, decays and production processes are enlarged enormously [1]. Being very similar at the quark level, some processes with the η - and η' -meson production in the bottomonium decays are very different from the ones in the charmonium sector of hadrons. So, a detail study of the η - and η' -meson production processes in bottomonium decays is necessary, in particular, the semi-inclusive ones, $Y(1S) \rightarrow \eta^{(\prime)} + X$, where X combines all the states with light hadrons. The first experimental analysis of this decay was done by the CLEO collaboration [2] in 2003 and was updated in 2006 [3]. The theoretical study of the decay with the η' -meson production was undertaken by A. Ali and A. Parkhomenko [4] where the process was considered at the tree level as the $Y(1S) \rightarrow g g g^* \rightarrow \eta' + g g g$ decay. The virtual gluon g^* produces the η' -meson via the effective vertex $g^* \rightarrow \eta' + g$ calculated within the perturbative QCD and appeared to be well enough to fit the experimental data [2] at large η' -meson energies. As the result, the values of the first Gegenbauer moments entering the quark and gluonic parts of the η' -meson light-cone distribution amplitude were obtained. Unfortunately, the improved CLEO analysis [3] based on the ten times larger statistics shows disagreement with the theoretical findings. To update the theoretical analysis, we suggest several improvements to the previous consideration, i. e., to use the strong coupling calculated within the fractional analytic perturbation theory (see, for example, [5]) and the $\eta' g g$ vertex function derived in the same approach. All these is also planning to apply to the $Y(1S) \rightarrow g g g^* \rightarrow \eta + g g g$ decay as it was not yet considered previously in such a framework. The first preliminary results are presented in this conference. It is interesting if the BaBar and Belle collaborations will perform an analysis similar to the CLEO one [2,3] as their $Y(1S)$ -meson data collected are larger the CLEO ones and the η - and η' -energy distributions can be obtained with more bins and smaller uncertainties.

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Semiclassical Theory of the Landau-Teller Model

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A model of atom-diatom inelastic collisions was first proposed by Landau and Teller in 1936 [1]. They studied the vibrational-translational energy exchange in diatomic gases, treating the diatomic molecule as a harmonic oscillator and considering the vibrational quantum of energy $\hbar\omega$ to be much smaller than $k_B T$. The Landau-Teller problem was solved subsequently in terms of quantum mechanics. During the last 80 years many approaches were applied in order to calculate vibrational transition probabilities for the Landau-Teller model. In 1970 William H. Miller formulated a semiclassical theory of molecular collisions based on the exact solutions of the classical equations of motions (numerically obtained trajectories) which are used to construct a semiclassical approximation to the quantum mechanical transition probability. Numerical calculations of these semiclassical expressions showed good agreement with quantum results in some cases. In order to carry analytic calculations Miller and Smith [2] suggested to apply a symmetrized first-order perturbation theory to the semiclassical expressions, satisfying microscopic reversibility. Recently Eli Pollak [3] proposed to use second-order perturbation theory in order to include the back-influence of the oscillator's motion on the energy transfer. He also symmetrized the transition probabilities. The aim of my work was to carry out numerically exact calculations of the semiclassical transition probability following the same symmetrization used by Pollak did and compare the results with second order perturbation theory and the numerically exact quantum computations. To simplify, using a slightly different simplified symmetrization procedure, I found that indeed second order perturbation theory improves the semiclassical approximation as compared to the numerically exact semiclassical results.

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Dielectric Permittivities of Gold and Silicon. Calculation of Casimir energy

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Casimir effect describes interaction between two uncharged conducting plates separated by a vacuum gap. It was predicted in 1948 by the Dutch physicist Hendrik Casimir [1]. He derived the attractive force between two parallel plates placed in vacuum at zero temperature. The case studied by Casimir represents an ideal model. This approximation is valid when one examines a system of two metal plates at distances much larger than λ_0 , with λ_0 being a characteristic length.

In 1955 Evgenii Lifshitz studied interaction between two dielectrics with arbitrary dielectric properties due to fluctuations of electromagnetic field [2]. He derived explicitly the result for two dielectric semispaces separated by a vacuum slit now called the Lifshitz formula [2]. Lifshitz also considered cases of small and large distances compared to λ_0 , studied temperature dependence.

Generally it is sufficient to know dielectric permittivities of the materials, geometry of the objects and temperature of the system in order to evaluate the interaction energy between two objects separated by a vacuum gap. Dielectric permittivities of most materials can be measured experimentally in a certain frequency range (usually from infrared till X-ray). The Lifshitz formula contains an integral (or the sum) along an infinite frequency interval [2], therefore the dielectric permittivity function has to be determined along the whole frequency axis. Nowadays various models of dielectric permittivity function exist, however, the question of finding the physically reasonable model for evaluation of the Casimir force still leads to disputes in scientific community.

We consider two materials frequently used in Casimir experiments: gold and silicon. We managed to construct dielectric permittivities functions of Au and Si on the basis of experimental data and analysis of classical models. Our main goal was to approximate experimental data and to continue these functions analytically along the whole frequency axis by choosing physically reasonable asymptotic conditions.

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Modeling and Analysis of the Electronic Structure of Ytterbium Fluoride

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Control of the physicochemical state of the lanthanide atom in the volume of the sample using X-ray emission spectroscopy is limited, primarily the difficulty of interpreting the experimental data. Establishing communication between the measured X-ray spectrum and shift state of the atom in the compound by direct simulation of the electronic structure and spectra are very promising. However, this approach has not yet been widely adopted both because of the complexity of traditional schemes emergency relativistic calculations solids and other complex objects, and because of numerical instabilities chemical shifts estimates small compared with the energy ray transitions. We propose an effective method for determining the chemical shift [1] by calculating the electronic structure of chemical compounds using relativistic pseudopotential [2] and the procedures for restoring the posterior wave functions near atomic nuclei [3].

The main advantage of this method is a fully relativistic (four-component) description of the inner shells between which the x-ray transition is achieved on the basis of a two-component (including spin-dependent interactions), or even one-component (scalar-relativistic) calculation of the electronic structure of the compounds with the explicit consideration of only the valence and subvalence shells.

The results of calculations of chemical shifts $K\alpha$ -lines of ytterbium trifluoride relative difluoride ytterbium are presented. This research was done at the expense of the grant of the Russian Scientific Fund (project №014-31-00022).

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Non-Diagonal Green Functions for Disordered Systems

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Electronic properties of disordered systems are of great importance for the development of fundamental science as well as for applications. One of the interesting fundamental effects discovered in disordered lattice is Anderson localization, when quantum interference completely suppresses the diffusion of particle in random potential. Although this phenomenon was predicted more than 50 years ago it is still attracts attention in various domains of physics [1].

Useful approach for investigation of Anderson localization within the framework of tight-binding model is the recursion method which allows to calculate diagonal on atomic sites i matrix elements of electronic Green function G_{ii} as infinite continued fraction [2, 3]. Imaginary part $\text{Im}G_{ii}(w-i0)_i$ determines the density of states localized on atom i , whereas analysis of asymptotic behaviour of the sequence of recursion coefficients gives information about localization of electrons in real space. It is worth to note that non-diagonal on atomic sites Green function G_{ij} give amplitude of transitions between i and j sites and therefore have to contain direct information about localization of electronic states. Non-diagonal Green function can be calculated within the framework of standard recursion method using following relation:

$$G_{ij} = \langle x_i | G | x_j \rangle = \frac{1}{2} \left(\left\langle \frac{x_i + x_j}{\sqrt{2}} \left| G \right| \frac{x_i + x_j}{\sqrt{2}} \right\rangle - \left\langle \frac{x_i - x_j}{\sqrt{2}} \left| G \right| \frac{x_i - x_j}{\sqrt{2}} \right\rangle \right)$$

Here $|x_j\rangle$ is the basis vector localized on site x_j . Thus non-diagonal Green function can be calculated via diagonal ones but with another initial vector used in recursion procedure. Non-diagonal Green functions G_{ij} has been calculated for the system with random on site energies (on-site energy uniformly distributed in the interval $[w_1, w_2]$) for different distances $||x_i - x_j||$ and varied width of energy distribution $|w_2 - w_1|$.

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Quantum Few-Body Problem

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There are many examples of quantum-mechanical systems of several particles in nuclear physics, atoms and molecules in atomic physics. Description of these systems is a difficult task and requires the use of different methods for solving the Schrödinger equation of several particles. The study of this class of problems can be started with a simple two-particle systems [1], the results can be generalized to more complicated structures.

There is a class of quantum systems that represent special interest for studying. They are characterized by weak interactions between the particles and by the wave function spreading over large distances exceeding the radius of the Bohr orbit in the tens and hundreds times. This is the condition for so-called Efimov state [2]. These systems characterized by the presence of the resonance condition for three particles, in spite of the weak interaction of pairs of particles.

The purpose of this paper is to present different approaches to solve the problem of few particles. There has been also developed and implemented method of solving the Schrodinger equation with a special DVR function expansion [3] of the wave function. The binding energies and wave functions have been obtained for compounds of helium, sodium and lithium.

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Linear and Nonlinear Contributions to the Zeeman Splitting in Highly Charged Ions

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Substantial interest in theoretical investigations of the g -factor of highly charged ions is motivated by the high-precision experiments, both recently performed and anticipated in the near future. Today's highlights in this field are the most accurate determination of the electron mass [1], the most stringent test of the many-electron QED effects in the presence of magnetic field [2,3], and the isotope dependence of the g -factor of lithium-like calcium [4]. Planned experiments with heavy ions will give an opportunity for independent determination of the fine-structure constant [5]. Measurement of the Zeeman splittings of $2p_{1/2}$ and $2p_{3/2}$ states in boron-like argon is presently performed at GSI. In this case, the effects of second and third order in magnetic field have to be taken into account [6,7]. We present an effective computational approach for evaluation of various contributions to the linear and nonlinear Zeeman effect. The electron wave functions in the combined nuclear electric and external magnetic fields are constructed within the perturbation theory on the basis of the DKB-splines [8]. The one-electron and two-electron matrix elements are evaluated with these functions. The corresponding contribution to the k^{th} - order Zeeman effect is obtained through the k^{th} derivative with respect to the magnetic field.

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Radiative Recombination of Electrons with Bare Nuclei

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Radiative electron recombination is one of the basic processes which occur in electron-ion and ion-atom collisions. Various approximations are employed for description of the electron recombination in electron-ion and ion-atom collisions [1]. In the present work the cross sections for relatively simple process of radiative electron recombination have been calculated within the exact relativistic theory [2-4] as well as within several approximations. Accuracy of the employed approximations is investigated in details.

The processes of electron recombination with bare nuclei in collisions of the bare nuclei with free electrons and with light atoms are considered. The accuracy of the plain waves approximation [1] where the incident electron is described as a plain wave is investigated. The relative contributions of the electron recombinations to the ground (1s) state and to the low-lying states (2s and 2p) are compared. The characteristic values of the angular momentum transfer and the characteristic radius of the interaction for the processes of radiative electron recombination are discussed. The contribution of the target properties in the ion-atom collisions are studied.

The study is performed for a wide variety of the bare nuclei ($10 < Z < 100$, where Z is the nuclear charge) and energies of the incident electron.

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Nonperturbative Treatment of the Zeeman Effect in Highly Charged Ions with Nonzero Nuclear Spin

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Investigations of the Zeeman splitting of the hyperfine-structure levels in few-electron ions can serve for precise determination of the nuclear magnetic moments [1,2]. We present relativistic calculations of the g-factor and the coefficients of the Breit-Rabi formula for $n = 1$ and $n = 2$ energy levels in few-electron ions. In contrast to previous calculations [3-6], where the magnetic interaction was treated as a perturbation, we start with Dirac equation in the presence of external magnetic field, which is solved within the dual-kinetic-balance approach [7]. The results for $1s$ and $2s$ states are in agreement with the previously published values [3-5]. The results for $2p (1/2)$ and $2p (3/2)$ states provide the theoretical basis for future experiments with boron-like ions.

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H. Biophysics

Conformational and Optical Properties of Novel Linear Cationic Polymers

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The novel polymer and polymer composite materials play an important role in the development and implementation of new methods and approaches for the creation of nanostructures and multicomponent systems. Properties of novel linear cationic polymers and copolymers allow to use them in different applications: for example as a vector for controlled delivery of genetic material or drugs into cells.

In this study the properties of novel cationic polymers with varying chemical structure (Fig. 1) in a wide range of the molar masses (8000 – 130000 g mol⁻¹) in solutions were investigated by the methods of intrinsic viscosity, densitometry, refractometry, dynamic light scattering and flow birefringence. Translational diffusion coefficients, refractive indexes and intrinsic viscosities of samples were found. The values of the molecular weights were calculated. The values of the optical shear coefficients were obtained. Contributions of optical microform and macroform effects to the observed flow birefringence are analyzed in detail. The intrinsic optical anisotropy of segment and intrinsic optical anisotropy of the monomer unit of the polymer are estimated.

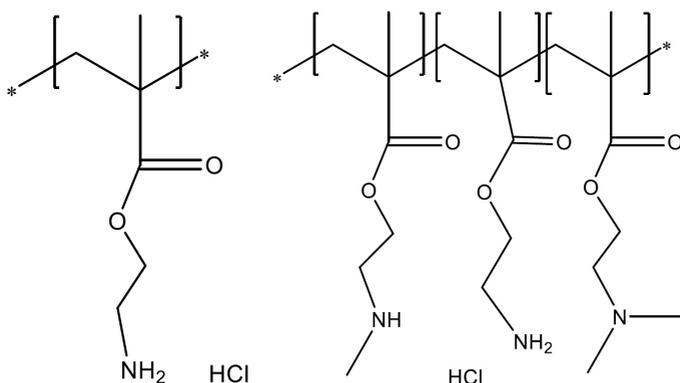


Fig. 1. Structures of new linear primary and tertiary amines containing methacrylates.

Acknowledgements. This research was supported by a grant from the Russian Science Foundation (project №16-13-10148). A part of experiments were performed on the equipment at the “Center for diagnosis of functional materials in medicine, pharmacology and nanoelectronics of St. Petersburg State University”.

IR-spectroscopy of DNA with cis- and trans- DDP

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The aim of our research is to establish the relationship between changes in the infrared spectra of DNA-diamindichlorplatinum (DDP) complexes solutions and the interaction of specific atomic groups. We compare the spectra of the DNA solutions (the concentration is 20 mg/ml) with different ratios DDP/DNA phosphates (1/10, 1/20, 1/50, 1/100). The shift of bands 1562 cm^{-1} and 1576 cm^{-1} to the region of lower wavenumbers due to the DNA interaction with DDP is observed. This fact indicates for the change in frequency of vibrations the $C = N7$ and $C = N$ (H2) in guanine. In the case of cis-DDP the band at 1575 cm^{-1} is shifted more than in the case of trans-DDP. Also the band intensity (1562 cm^{-1}) decreases with increasing of platinum concentration. Therefore it is possible to conclude that the interaction of cis-DDP and trans-DDP with the guanine base leads to the above changes in the spectrum. In the case of cis-DDP-DNA complexes the band at 1678 cm^{-1} (associated with vibrations $C6 = O$ in guanine) also strongly shifts to lower wavenumbers. These changes may be caused by the formation of hydrogen bonds between the amino-group of cis-DDP and the oxygen atom of the guanine (O6).

In the case of trans-DDP-DNA complexes the band 1678 cm^{-1} shifts insignificantly. The band 1643 cm^{-1} (associated with vibrations of the thymine ring) shifts in the case of cis-DDP-DNA complexes and its intensity decrease with increasing of platinum concentration.

Besides, in the case cis-DDP-DNA complexes the shift of band 1698 cm^{-1} to region of longer wavelengths indicates the changing of frequency $C2=O$ vibrations in thymine. The increase in intensity of this band with increasing of platinum concentration is observed. These spectral changes can be caused by the changing of interactions between thymine and adjacent atomic groups binding with DDP. These changes indicate probably for the formation of intra-strand and inter-strand crosslinks in the DNA molecule.

In the case trans-DDP-DNA complexes noticeable shifts (taking into account the error) of bands 1643 cm^{-1} and 1698 cm^{-1} is not observed. It is possible to conclude that interaction with trans-DDP does not lead to structural changes of double spiral DNA.

Molecular Dynamics Simulation of the Structural Properties of P3HT Chain in a Helical Conformation

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Regioregular poly-3-hexylthiophene (P3HT) is a polymeric semiconductor widely used in the field of organic electronics. The structure of polymer matrix significantly affects the efficiency of P3HT-based organic photovoltaic cells. The structure of bulk P3HT sample is usually described as a combination of crystalline and amorphous domains. The most common representation of the P3HT crystalline domain structure is believed to be layers of parallel P3HT chains in elongated conformation. However Kiriy et al. [1] suggested the potential existence of the helical conformation of P3HT chains.

The aim of this study is to investigate the potential influence of temperature regime, amorphous polymer surrounding, and electrostatic interactions on structure evolution of a single P3HT chain in a helical conformation via the molecular dynamics-based simulations using the GROMACS software package. The interactions in the systems under investigation were described by the Gromos53a5 and Amber99sb force fields [2]. According to the study, when using the Gromos force field the helical chain is stable in vacuo at room temperature, but it promptly collapses at elevated temperatures. The destruction of the structure in the presence of the amorphous surrounding takes significantly longer time when compared to the vacuo conditions. The electrostatic interactions do not substantially affect the stability of the P3HT helical structure. When using the Amber force field a ‘frozen’ structure was observed at temperature above the P3HT melting point, indicating that the description of P3HT using the Gromos force field is more adequate.

Acknowledgements. This work was supported by the Russian Foundation for Basic Research (grant № 15-03-07614). The simulations were performed using the computational facilities of the Institute of Macromolecular Compounds, Russian Academy of Sciences, and the ‘Chebyshev’ and ‘Lomonosov’ supercomputers at Moscow State University.

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Coil-to-Flower Transition in a Linear Polymer Chain Inserted into a Brush Made of Starlike Macromolecules

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The layers of macromolecules grafted to an impermeable surface, or polymer brushes, belong to the most studied polymer systems. Among the diverse applications of polymer brushes one of the most interesting is their use as “matrices” for molecular switches. The idea of such a “molecular switch” consists in inserting a single polymer chain into a polymer brush. If the chain is different from the macromolecules forming a brush it could undergo a dramatic conformational transition under environmental change (such as a change in temperature, pH, etc.).

In the present study we investigated the conformational properties of a linear chain inserted into a planar brush made of arm-grafted polymer stars. The chemical structure of the inserted linear polymer chain is identical to the macromolecules forming the brush. Using the Scheutjens–Fleer self-consistent field numerical method it was shown that short chain (shorter than a double star arm length) or a longer chain inserted into a sparsely grafted brush is in the coil-like conformation. A long chain in a densely grafted brush acquires a “flower” conformation with an extended “stem” and a coil-like “head”. The coil-to-flower transition in the linear chain can be initiated either by increasing the stars grafting density, increasing the chain length, or by amelioration of the solvent quality. The latter means that the system can operate as a thermo-sensitive molecular switch because the solvent quality is temperature-dependent. The observed coil-to-flower transition has the features of the first order phase transition. It occurs sharply via coexistence of two states (the “coil” and the “flower”), which is expressed in the form of a bimodal linear chain end distribution.

Acknowledgement. The work was supported by Russian Foundation for Basic Research (grant 14-03-00372a).

Electro-Optics of Comb-Like Polymers in Organic Solvent

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A series of studies of the hydrodynamic and conformational properties of comb-like polymers with ionically bonded side chains in organic solvent, depending on the synthesis conditions and the structure of the lateral fragment has recently appeared [1-2]. The equilibrium and non-equilibrium electro-optical properties of the poly(cetylammonium-2-acrylamido-2-methylpropanesulfonate) (CA-PAMPS) in the range of molecular masses $(2.0-0.1) \times 10^{-6}$ Da in dilute solutions in chloroform were estimated by electric birefringence (Kerr effect).

The acquired results indicate that the Kerr constant (K) is dependent on the molecular mass (M) in a power-law behavior ($K \sim M^a$) in the range of Gaussian coil conformations. The earlier studied comb-like polymers [3-4] also represented power functions of K (M). In the future the detailed consideration of this issue is essential for the development of fundamental concepts on the electro-optical effect in solutions of comb-like polymers.

Studying of process of the relaxation of the electric birefringence after the end of the rectangular-wave electric field has allowed estimating the hydrodynamic sizes of relaxing macromolecules. The results were compared with the available experimental data obtained previously by dynamic light scattering [2] and a general agreement was found.

Acknowledgements. This work was supported by grants RFBR (project № 15-03-08506a) and “Center for diagnosis of functional materials in medicine, pharmacology and nanoelectronics of St. Petersburg State University”.

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Electro-Optical Properties of Metallomesogen Complexes

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Metal-containing liquid crystals (LC) is metallomesogen - coordination compounds of transition metals with organic ligands, which can also contain counterion. Synthesis of metallomesogenic LC's enriched liquid crystals chemistry by a variety of geometric shapes of mesogenic molecules and its unusual physical properties of the mesophases, due to the presence of the metal atom as part of mesogenic molecules. Interest in the study of such LCs is due to a wide wide prospects of its practical applications.

The study was aimed on the investigation of isotropic-liquid phase of the LC melt, in order to identify the relationship between the molecular structure, the sign and the magnitude of the electro-optical constant.

A smectic complexes of rare earth metals, with different length of aliphatic chains of ligands were investigated using polarizing microscopy, and electric birefringence (Kerr effect) techniques. Earlier in our publication it was shown that the electro-optical properties of such complexes, as well as the properties of the normal calamitic liquid crystals can be described using theoretical models, the Landau - De Jean [1]. It was established that value and sign of the electro-optical constant $K(T-T^*)$ is changing with variation of the length of aliphatic chain of ligands.

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Study of DNA Interaction with Short Peptides AEDG and EDR by Spectral Methods

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Some short peptides are known as natural bioregulators for different physiological processes. Indeed, the human body contains different short peptides involved into the regulation of vital processes such as gene expression, cells proliferation and differentiation. Peptides are also the important signaling molecules [1, 2]. Study of the molecular mechanism of the interaction of short peptides with DNA, which is a possible molecular target for these peptides is necessary for molecular biology and biophysics.

Peptides AEDG, epithalon, and EDR, pinealon, were studied. These peptides (Fig. 1) were obtained in St. Petersburg Institute of Bioregulation and Gerontology. The possibility of binding of short peptides with high molecular weight calf thymus DNA was regarded in this work. The analysis of DNA melting curves was used to study DNA - peptides complexes. Spectrophotometric method was used to obtain the absorption spectra of the objects under study.

The results have shown the interaction of short peptides with DNA. DNA melting temperature was 65 °C. In the presence of epithalon and pinealon DNA melting is observed 60 °C and 57° C, respectively.

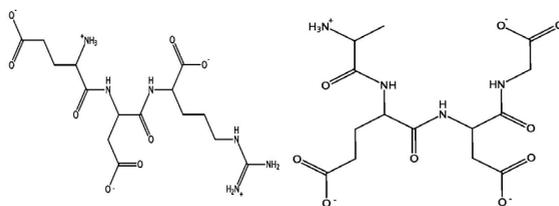


Fig. 1. EDR and AEDG.

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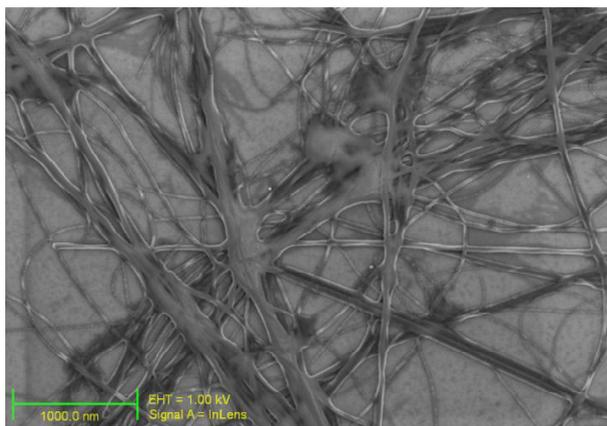
DNA Complexes with Silver Compound Containing Phenanthroline

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Complexes with metal ions have a great potential for applications in medicine. These coordination complexes can modify DNA in tumor cells. Phenanthroline is also known as antimicrobial and antitumor agent. The investigation of DNA interaction with silver compounds in a solution can provide the molecular model of their biological activity. The interaction of silver compound with DNA gives the silver links to DNA, and the reduction such silver on DNA strands results in creation of conductive structures. This technology offers great opportunities in the field of nanoelectronics.

In this work, we have studied the interaction of acetate bis(1,10-phenanthroline) silver(I), further Ag-phen, with thymus DNA using UV spectroscopy, CD, viscometry, flow birefringence methods. The DNA melting in the presence of Ag-phen was also studied. The result obtained for Ag-phen were compared with those for DNA binding with free silver ions and free phenanthroline. We have obtained a way for the creation of thread-like DNA structures with reduced metal. SEM and AFM images for these structures were obtained. The presence of metallic silver in these structures was confirmed. We have also compared these structures with DNA complexes with silver nanoparticles. In addition, the data on the mechanical properties of DNA-phenanthroline-silver structures was obtained. The electrochemical properties of these structures were also investigated.



DNA-phenanthroline-silver structures.

Theoretical Study Polymer Brushes Structure Made of Arm-Grafted Polyelectrolyte Stars

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Polymer brushes are the monolayers of macromolecules densely grafted onto an impenetrable surface. Planar brushes formed by arm-grafted polyelectrolyte stars with a fixed charge distribution are investigated by using the Scheutjens-Fleer self-consistent field numerical approach. It was shown that stars in the brush are divided into two-populations: The fraction of stars has extremely extended "stem" – the grafting arm – and their free arms extend toward the brush periphery. The rest of stars are weakly stretched and occupy the subsurface layer of the brush.

A simple mean-field theory is developed to describe the two-population structure of star brushes. It was shown that increasing the grafting density, the number of arms, or the degree of arms' ionization, as well as decreasing the concentration of salt leads to the increase of the brush height and segregation of stars into two "populations". The results of the theory are found to be in a good quantitative agreement with the results of the self-consistent field calculations.

Acknowledgement. The work was supported by Russian Foundation for Basic Research (grant 14-03-00372a).

Study of the Hydrodynamic Properties of Cross-Linked Polymers Based on Polyn-Acryl-11- Amidoundecanoic Acid

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Surfactant polymers are capable of forming intra- and intermolecular organized structures (e.g., micelles) receive great attention from researchers working in the field of polymer science.

Micelles (including polymer micelles) are very sensitive to external factors. Namely forms of micelles (sphere, cylinder, etc.) and size (aggregation number) are strongly dependent on temperature, ionic strength, pH of the solution, the presence of an organic solvent and other factors. It is possible to control the shape and size of the macromolecules by varying these factors at the stage of synthesis, and further to create new polymer structures with desired properties. By adding the crosslinking agent which is capable of forming a chemical bond between the different parts of the macromolecule in the synthesis, it is possible to further fix the size and shape of the resulting polymer nanoparticles.

Poly(N-acryl-11- amidoundecanoic acid) (PAAU-H) and its sodium salt (PAAU-Na) represent very promising materials for molecular cores in constructing nanoparticles with surface functional groups. Typically they are used for encapsulation of various biological preparations. The influence of quantity of cross-linker incorporated in polymerized micelles (from 1 and up to 20 mole percent) was studied by means of hydrodynamic methods to determine the conformational status of the polymerized micelles. This goal was achieved by polymerization of the AAU-Na in the presence of a rigid short crosslinking agent - methylene-bis-acrylamide.

Particular attention was paid to the analysis of both the size and the shape of the formed particles by using unique combination of methods of molecular optics and electro-optics.

Acknowledgements. This work was supported by the Russian Foundation for Basic Research (grant 15-03-08506a). A part of experiments were performed on the equipment at the “Center for diagnosis of functional materials in medicine, pharmacology and nanoelectronics of St. Petersburg State University”.

Poly (methacrylamido-D-glucose) Copolymer Modified by Cyclodextrin

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The solution properties of novel synthetic biocompatible polymers have been investigated. Copolymers of 2-deoxy-2-methacrylamido-D-glucose with acrylic acid modified by β -cyclodextrin (MAG-AA-CD) or cholesterol (MAG – AA – Chol) were the objects of the study by the methods of viscometry, refractometry and dynamic light scattering in 0.2 M NaCl. Such macromolecular parameters as translation diffusion coefficient D , hydrodynamic radius R_h , and intrinsic viscosity value $[\eta]$ were determined. Also there were analyzed the conditions for the study of complex formation between MAG-AK-CD and MAG – AA – Chol. It was shown that very special procedure of the complex formation demands for the experimental study of MAG-AK-CD and MAG – AA – Chol interaction by the method of dynamic light scattering.

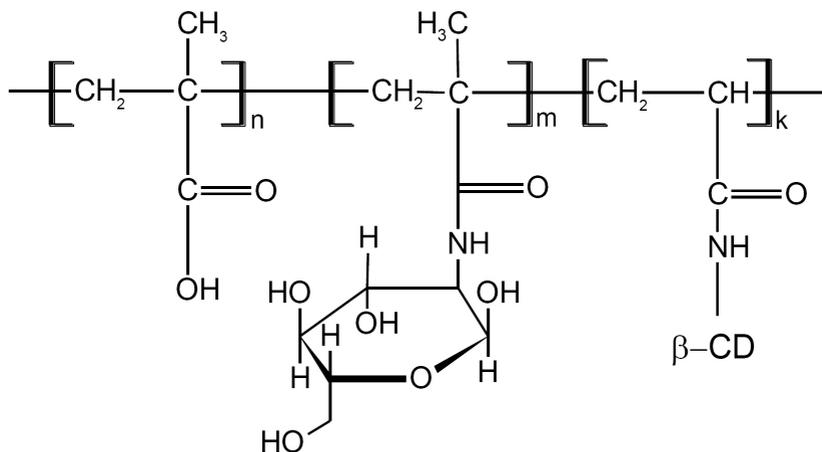


Fig. 1. The structure of poly (methacrylamido-D-glucose) copolymer modified by cyclodextrin (CD).

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Secondary Structure of Proteins Revealed by FTIR Spectroscopy

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IR spectroscopy is a very powerful method for the molecular structure analysis. This method is widely applied for investigating of proteins in solutions, fibrils, in solid (lyophilized) state and in whole biological samples [1]. There is a correlation between definite bands in IR-spectra of polypeptides and their secondary structure. Amid I band (1600 cm^{-1} – 1700 cm^{-1}) which corresponds to C=O, N–H and C–N oscillations is the most informative one [1, 2]. The decomposition to Gaussian contours of Amid I band was employed in this research to get information about the content of different forms of proteins secondary structure.

In this work IR-spectra were received and secondary structure of globular proteins (HSA (human serum albumin), OVA (ovalbumin), BSA (bovine serum albumin)) in water solution and in lyophilized state was determined. Analogically the secondary structure of amyloid fibrils of yeast prion and of proteins in biological samples: human hair and nails (consisted mainly of α -keratins) and egg white (60% OVA content) was obtained. These data satisfactorily agreed with results revealed by other methods of protein secondary structure investigation [3-5].

In spite of the presence of admixtures the content of secondary structures of native egg white was close enough to pure OVA. Changes in secondary structure of OVA during denaturation (in boiled egg) are also fixed in IR-spectra reliably. So IR-spectroscopy is a quite promising method which don't require complicated sample preparation for diagnosis of different diseases affecting protein structure [6].

Acknowledgements. This work was supported by SPbSU (11.37.290.2015). Scientific research were performed at the Center for Optical and Laser Materials Research of Research park of St. Petersburg State University.

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Small Interfering RNA and DNA Interaction with Azobenzene Containing Surfactant

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The interaction between cationic surfactants and nucleic acids has been studied extensively. DNA condensation that occurs in the solutions with cationic surfactants has appealed to scientific interest due to different applications of these compact particles. They are employed in biomedicine for the delivery of nucleic acids into cells. The interaction of surfactants with DNA in a solution has been scrupulously studied in connection with problem of gene transfection. In contrast, the delivery of small interfering RNAs (siRNAs), which is regarded as a powerful therapeutic tool and has been extensively discussed since the demonstration of RNA interference (RNAi) is still under discussion.

The goal of our study was to obtain novel data on binding of azobenzene cationic surfactant AzoTAB to DNA and siRNA in vitro. For siRNA the conditions of the formation of nanostructures in solution are determined, and we examined the efficiency of transfection for these systems using cell cultures.

Sigma Aldrich calf thymus (CT) DNA and Dharmacon GE siRNA were used. For delivery study AlexaFluor siRNA was used. Molar concentrations of nucleic acids were calculated from average molecular weight per phosphate of DNA 330 g/mol and of siRNA 321 g/mol. Nucleic acids were dissolved in Milli-Q Type I ultrapure water or in Sigma ultrapure water. Surfactant samples and scientific outline for this project were provided by Prof. S. Santer (University of Potsdam, Germany).

Azobenzene containing surfactants undergo trans- to cis- isomerization under UV irradiation (353 nm). Reverse cis-trans transition is induced by visible light (453 nm) or can be realized in darkness. Delivery of siRNA + surfactant systems was tested on MDCK cell line.

For spectral studies we used SF-56 spectrophotometer, low-gradient viscometer of Zimm-Crothers type and NanoScope IVa (Veeco) atomic force microscope (AFM) were also used for the characterization of complexes.

We examined binding of cationic agent (azobenzene containing surfactant AzoTAB) to the molecules of nucleic acids siRNA and DNA using UV-Vis and fluorescence spectroscopy. For DNA macromolecules of high molecular weight we also carried out a combined viscometry/flow birefringence study to examine DNA conformational changes upon binding with trans- and cis- isomers of the surfactant. For siRNA + surfactant systems we aimed to determine the conditions of gene vectors' creation by AFM observation and by testing the delivery on MDCK cell line.

I. Resonance Phenomena in Condensed Matter

Magnetic Resonance Susceptibility Weighted Imaging

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SWI (Susceptibility Weighted Imaging) - a relatively new imaging technique which was first described by Haacke and his colleagues in 2004 [1]. Most brand tomograph are not equipped with programs SWI imaging method.

In order to enhance the contrast of MRI use local magnetic field inhomogeneities that are caused by different values of the magnetic susceptibility of substances such as deoxyhemoglobin, iron and calcium. In this way, MR SWI mode allows you to visualize the traces of small hemorrhages after a long time, the deposition of iron-containing substances in certain brain structures, and contrasted the venous blood.

When we use the SWI, magnitude and phase images are combined program to obtain images with the contrast [2]. Such images are very sensitive to venous blood, hemorrhages and accumulations of iron.

The difference SWI program from the standard program T2*- contrast is to use the phase data to construct the images. [3]. This leads to a greater sensitivity to local changes in the magnetic susceptibility. Consequently, this method has a greater sensitivity to the detection of foci of such a varying magnetic susceptibility.

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Effect of Preparation Method on Local Structure of Copper-Exchanged Mordenites: ^1H , ^{27}Al , ^{29}Si MAS NMR Study

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Composite materials in which nanoparticles of transition metals are introduced into the voids of a crystal matrix, such as a zeolite, are becoming more widely used [1,2]. These materials have unique magnetic, optical, electrical and other properties.

It is well known that -introduction of copper into -zeolites considerably improves their catalyst activity [3]. Despite the fact that these materials are thoroughly investigated in the last decade, the localization of copper ions in the zeolite matrix and their valence state is still not completely defined.

Magic Angle Spinning Nuclear Magnetic Resonance (MAS NMR) is a powerful method for a local probe. In this contribution we report on our results of the experimental study of a series of copper exchanged zeolites with mordenites structure carried out using ^1H , ^{27}Al and ^{29}Si MAS NMR.

The samples were synthesized from Na-mordenites with a molar ratio $\text{SiO}_2/\text{Al}_2\text{O}_3 = 13$ by two methods (conventional and microwave) with different copper exchange degree (for more details see Ref. [4]). And one of the purposes of the present study is to follow how the method of synthesis and number of copper-exchange procedure affects the local environment of a selected nucleus.

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Visualizing of Acoustic Standing Waves by Cavitation

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As a rule acoustic waves are invisible. But it is possible to use acoustic cavitation to visualize acoustic standing waves in liquid.

Acoustic cavitation is the growth and collapse of vapor bubbles due to the fast changing pressure in the field of ultrasonic wave. Cavitation structures frequently appear as a cavitation cloud [1]. The cloud consists of vapour and gas bubbles. Gas bubbles congregate in nodes of standing wave and vapour bubbles in antinodes. Cavitation picture is very unstable because the vapor bubbles collapse and disappear after each period of pumping wave [2].

In the course of experiments we obtained numerous photo shots of acoustic cavitation structures (Fig. 1).



Fig. 1. Cavitation cloud.

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Molecular Dynamics of Ionic Liquid (Methyl-Octyl Imidazolium Chloride) in Mixture “Water – Glycerol”

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Ionic liquids (IL) are referred to as ionic compounds which are characterized by a melting point below 100°C. Cations determine mainly physical properties of IL (melting point, viscosity, density), whereas anions determine chemical properties. Since the physical and chemical properties of ILs can be adapted to the specific conditions by careful selection of types of cations and anions, IL have become widely used in many scientific and industrial applications [1-3].

This research is devoted to the study of the effects of glycerol media on the micellization of IL in aqueous solutions that is of great interest for cosmetology, pharmaceuticals and other industries. One of most commonly used types of ILs nowadays is based on imidazolium ring due to their unique chemical properties and easiness of variation of cations and carbon backbones. The significant work in this aspect has been undertaken and the latest results are summarized in the present paper.

The research of the system IL-glycerol-heavy water was carried out using NMR technique. The existence of molecular aggregates in glycerol-water media was confirmed. Aggregation process is not abrupt and takes place in a wide concentration range. Isotopic exchange of H ↔ D was investigated. IL aggregation degree affects the rate of this exchange. Micellization concentration range for this system was obtained: 2 points of interest reveal in concentration range from 0.05 to 1.2 mol/l that may be referred to different formations of micelle. Glycerol molecules, as well as water molecules, form coordination sphere of molecular aggregates.

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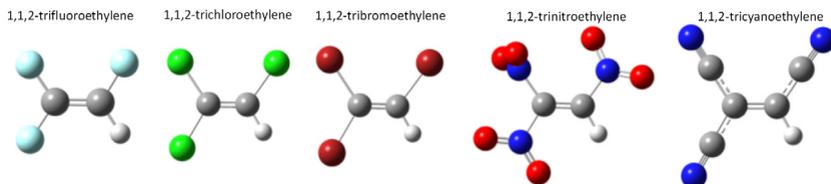
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Quantum-Chemical Calculations of Substituted Ethylenes as CH Proton Donors in Hydrogen-bonded Complexes

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The hydrogen bonds involving a CH-group are ubiquitous [1]. However, CH proton donors with sp^2 -hybridized carbon are less studied than other types of CH-donors [2]. It seems interesting to study the correlation between electron shell properties of free CH-acids and the geometric, energetic and spectroscopic properties of the H-bonded complexes formed with various proton acceptors.



As the main object for this study we have selected 1,1,2-trisubstituted ethylenes (see Fig.). We show the following.

1) In the sequence of substituents F, Cl, Br, CN, NO_2 the strength of the complexes formed by substituted ethylenes with chloride-anion increases. This tendency is accompanied by the following geometric and spectral changes: C...H distance increase, H...Cl distance decrease, deshielding of the bridging proton and decrease of the spin-spin coupling constant $^1J_{\text{CH}}$. All these characteristics correlate well with the proton affinity of the corresponding ethylene and the partial atomic charge on the CH proton.

2) To further characterize the electron shells of substituted ethylene molecules and their ability to act as proton donors we have carried out preliminary calculations of ethylene complexes with Helium atom. The most informative spectroscopic parameter appears to be the chemical shift of ^3He , which correlates with the electron density on CH-proton. We propose to use the chemical shift of ^3He as a measure of proton donating ability of CH acids in a homologous series.

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Hydrogen Bonding Between Phosphinic Acids and Pyridines: Theoretical Study of CSA Tensor Dependence on Proton Position

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In modern literature, extensive data is accumulated on the effect of substituents on the absolute value of the isotropic ^{31}P NMR chemical shift of organic molecules in liquid solutions [1]. However, the effects of hydrogen bond formation on ^{31}P NMR chemical shifts of phosphinic acids (R_2POOH) is much less studied. The interpretation of spectral ^{31}P NMR data in terms of interatomic distance in H-bonded complexes remains an open question.

This work is devoted to the study of intermolecular OHN hydrogen-bonded complexes formed between several phosphinic acids (R_2POOH , $\text{R} = \text{H}$, Et, Ph) and substituted pyridines (Fig. 1). The dependence of chemical shift anisotropy (CSA) tensor components and of its isotropic values on several processes is considered: gradual proton transfer towards the nitrogen atom of the base, internal rotation of R substituents of the acid, formation of weak H-bonds with the $\text{P}=\text{O}$ group of the acid. Complexes were studied theoretically by means of DFT calculations and experimentally by the low-temperature ^1H and ^{31}P NMR spectroscopy in polar aprotic solutions.

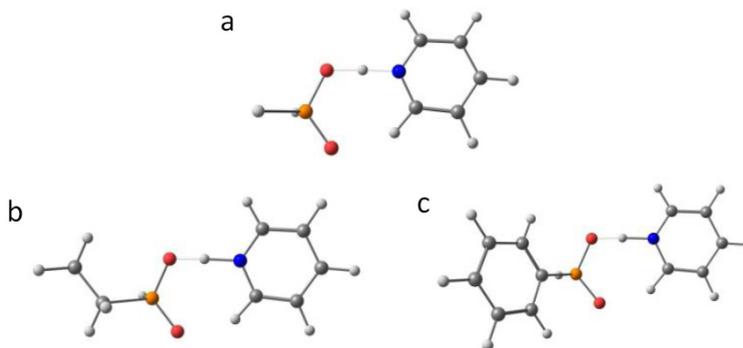


Fig. 1. Examples of hydrogen bonded complexes of (a) phosphinic, (b) dimethylphosphinic and (c) phenylphosphinic acids studied in this work.

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Indexing Layered Perovskite-Like Structures

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The search for alternative sources of energy in our time is one of the priorities of modern science. One of such source is the production of hydrogen from water using a solar energy, but this process is not naturally goes spontaneously, therefore it requires to use photocatalysts, which are layered perovskite-like structure.

The structures represent a huge class of compounds and their distinctive characteristic is the presence of layers consisting of BX₆ octahedra (B - cation, X - anion), or its fragments.

Perspectives of layered perovskite structures as photocatalysts consist in their different properties, one of which is the intercalation of water in the interlayer space. The result of this phenomenon is that the working surface of the photocatalyst is increased, and therefore its efficiency is increased. For registration of the capacity of intercalation can be used neutron and synchrotron radiation as this process is directly related to an increase in the lattice parameters.

In this paper, the two diffraction patterns were analysed: for H₂La₂Ti₃O₁₀ and H₂Nd₂Ti₃O₁₀ compounds. Presented samples were synthesized at the Chemistry Department of St. Petersburg State University, and the diffraction experiment was carried out on line BM01, ESRF. In order to determine the lattice parameters, the angles between them and the space group of the treated samples was conducted indexing, whereby the following results were obtained:

- H₂La₂Ti₃O₁₀: a = b = (3.8190 ± 0.0005) Å, c = (28.062 ± 0.008) Å;
- H₂Nd₂Ti₃O₁₀: a = b = (3.7980 ± 0.0005) Å, c = (29.347 ± 0.008) Å
- Crystal structure of both compounds - tetragonal.

The difference in distance is correlated with the fact that in the Nd sample ion exchange processes are going with more intense and generating hydrogen substituted compounds that can be intercalated.

In the future it is planning to analyze different layered perovskite-like structures for searching relationship between compound properties and crystal structures.

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Diffusion Weighted Imaging in Ultra-Low Magnetic Field

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Since protons in water molecules are a source of intense nuclear magnetic resonance signal, high water content in the human body (approximately 70%) provides successful clinical application of magnetic resonance imaging.

Contrasting of images by the certain parameters is a changing of the NMR images in dependence on the sensitivity to this parameter.

Contrasted images could be divided into two groups. The first one is parametric images, i.e. the images of the spatial distribution of the parameter, where the brightness is proportional to the value of the displayed parameter. And the second one is parameter-weighted images, where the brightness of the image is determined not only by the parameter of interest, but also by all other factors affecting the intensity of the NMR signal.

The most common imaging techniques are weighting on the relaxation times and diffusion weighting, which is far less widespread. In this case, the image weighting parameter is the self-diffusion coefficient. The features of water molecules diffusion can reflect a state of biological tissues. For medicine the great interest is presented in those cases when DWI (Diffusion Weighted Imaging) of a normal tissue differs from pathologically changed [1, 2].

We study the possibility of obtaining DWI in ultra low magnetic field [3]. The method of obtaining DWI represents a combination of methods for measuring self-diffusion coefficient and methods of spatial encoding in MRI. In this work the results of experiment on obtaining DWI at magnetic field 7 mT are presented, using the laboratory homebuilt nuclear magnetic resonance imager. For realization of the imaging pulse sequence the special programs were created in the LabVIEW environment.

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Charged Particles Identification by Time of Flight in the BM@N Experiment

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NICA (Nuclotron-based Ion Collider fAcility) is a new accelerator complex designed at the Joint Institute for Nuclear Research to study a special state of matter - hot and dense baryonic matter. One of the problems of experiments on accelerators is particles identification. The main goal of this work is to develop a method of the particles identification in Au+Au collisions.

Experimental data is based on the information from GEM and TOF-400 detectors – the coordinates of hits (points where particles went through) and time of flight from the interaction vertex to TOF-400 plane. After the first step of data analysis GEM hits combine with tracks. Using extrapolation with Kalman Filter the expected point of track intersection with next TOF-400 was found. The next step of the analysis is: closest TOF-hit brought into compliance with this track and its length is calculated. It allows us to calculate the mass of a particle. An assumption about the type of particle is based on mass.

The method was tested on the data is obtained from simulated events – Au-Au collision. In Fig. 1 shown calculated m^2 (mass²) depending on p/q (momentum/charge).

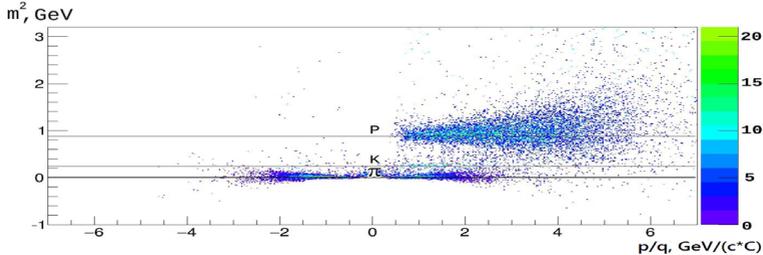


Fig. 1. Particle identification.

The results are analyzed for efficiency and contaminations (values used to evaluate the accuracy of identification).

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Research of the Structure of Micelles in Ionic Liquid Aqua Solution

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Ionic liquid is an important class of substances. Octyl-methylimidazolium chloride, that had been researched, is capable to form aggregates at special concentration in aqueous solution [1, 2]. The solution is simulated by molecular dynamics. Model of the system is shown in Fig. 1.

Pre-developed algorithm determines micelles at a fixed time. The algorithm finds such parameters as aggregate size, number of molecules in them.

Molecular systems, exceeded the critical micelle concentration 2 and 4 times, at the temperatures 298 and 322K, were analyzed. Development of systems has been investigated for 4649 ps.

It determines size of micelles and residence time inside the aggregates. Also it finds the average number and the proportion of ions included in micelles. Found values are similar to earlier findings [2].

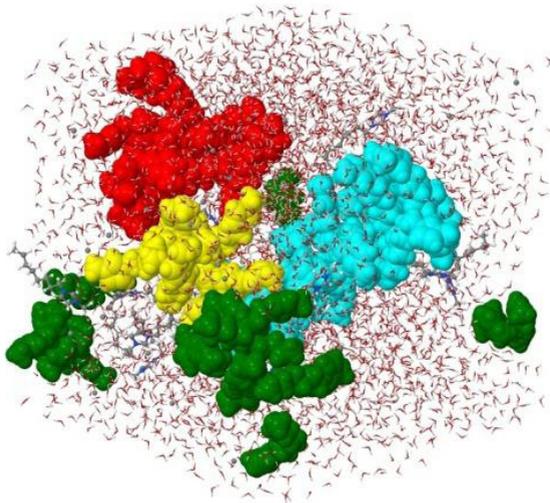


Fig. 1. Model of “Ionic liquid - water” solution.

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Development of Software for Operate of the Sample Temperature Control Unit

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Nuclear magnetic resonance (further NMR) is one of the most powerful and informative methods for the study of matter. When carrying out these researches, it is necessary to register temperature dependences of important NMR parameters (T1, T2, D, and also spectral characteristics, such as chemical shift, width of the NMR spectral lines) [1]. It is necessary to change the temperature of a sample placed in relaxometer probe head, in a wide range and to maintain it stable in the registration process.

To solve these problems at the disposal of the Department of NMR - relaxometer "ECHO 12" features developed in the laboratory unit temperature control, which is part of the PID controller "OWEN TRM-210", which provides high-quality implementation for thermostating samples requirements described above [2].

The aim of this work is to develop software for interacting PID control "OWEN TRM-210", which provides operate of the sample temperature control unit with the computer. And also to prepare the unit for software integration and software - hardware interface (SHI) "EchoSkan" developed in the LabView environment, with what and associated range of development environments.

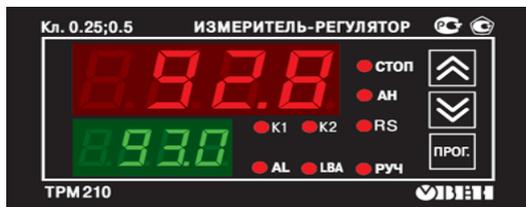


Fig. 1. Front panel "OWEN TRM-210".

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³¹P NMR Study of Self-Association of Phosphinic Acids in Polar Aprotic Solvents

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The molecules containing both proton donating and proton accepting groups are capable of forming hydrogen bonded self-associates (dimers, trimers, other aggregates). One of the classical examples of this behavior is given by phosphinic acids R_2POOH , which form in crystalline state either cyclic dimers or infinite chains [1]. Interestingly, the IR spectroscopic data indicate the unusually strong H-bonds in R_2POOH cyclic dimers [2]. In this work we attempt to study the equilibrium constant K of self-association of three phosphinic acids ($R = \text{alkyl, O-alkyl}$) at variable concentrations in polar aprotic solution ($CDCl_3$) by 1H and ^{31}P NMR spectroscopy (Fig. 1a), as well as NMR diffusion measurements and some DFT calculations (Fig. 1b).

Analysis of the obtained results allowed us to conclude that the simple monomer-dimer equilibrium model (Fig. 1c) is insufficient to describe the self-association process. We speculate that the formation of cyclic trimers and chains of various length play an important role at high concentrations of the acid. Further experiments are planned using low-temperature NMR in liquefied Freonic gases mixture CDF_3/CDF_2Cl as solvents.

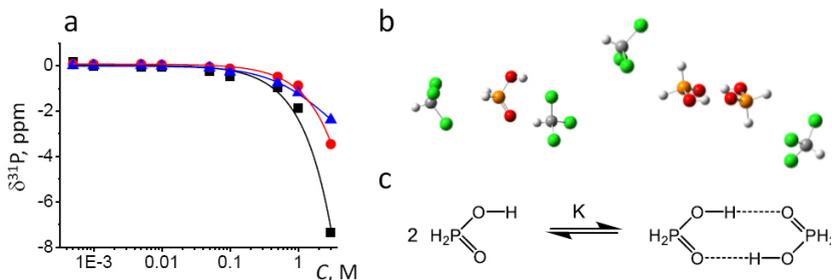


Fig. 1. *B-homo analogues of steroid estrogens.*

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Magnetic Resonance Measurements of Self-Diffusion Tensor in Ultra-Low Magnetic Field

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The first articles about diffusion influence on NMR experiments were published in the last half of the previous century [1]. Soon after that, special NMR techniques were elaborated. These techniques allowed researchers to measure the diffusion coefficient in a certain spatial direction. As a result of further development of the methods, a new one was formed. The method was called diffusion tensor imaging (DTI), and it allows us to quantitatively characterize the variation in diffusion, which occurs for different spatial directions in fibrous tissues. One of the most important application of the method is reconstruction of nerve fibers passes in human brains.

DTI is still an actively developing field of science. Most of DTI researches have been done in high magnetic field (3 T and higher) [2]. However, the same experiments in low magnetic field have their own advantages, for example, equipment mobility and wide range of possible equipment and software modifications. The low magnetic field techniques also can be used in order to decrease cost of testing new pulse sequences, training operators of MRI machine, and working with phantoms. It is especially useful for the DTI techniques because the diffusion coefficient doesn't depend on magnetic field strength.

In this research we have adapted the DTI algorithm to low magnetic field measurements. We conducted our research using homebuilt ultra-low magnetic field imager 7 mT, and the imager worked under control of a special program, written in LabVIEW.

As a result, in this work we have presented the measurements and visualization of the self-diffusion coefficient for fibrous plants in low magnetic field.

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Excitation Energy Transfer between DNA and Ag Clusters

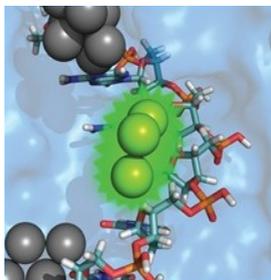
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Metal nanoclusters (NCs) is a special group of nanoobjects. The clusters of noble metals (gold, silver) is the most exciting direction in that research sphere. Silver NCs exhibit quite well luminescence parameters, such as high quantum yield, photostability and large absorption cross-section [1]. Because of that, silver NCs have huge potential in biology as molecular sensors or fluorescent markers for example. Furthermore, Ag NCs demonstrate the ability to harvest excitation energy from nucleobases, which can make them effective DNA-protectors from UV-light [2].

A purpose of this study was to estimate the quantity of the DNA bases from which the energy can be transferred to NCs. The silver nanoclusters were successfully synthesized in according with the protocol described by Volkov [3]. Then, emission and excitation luminescence spectra was obtained, analyzed and further calculations were performed.

Even with a quick look at the emission spectrum one can find two types of clusters: yellow and red ones. From the calculations, we have obtained the quantity of nucleobases for each cluster type: 25 – for the red one, 16 – for the yellow one.



Optimized structure of DNA–Agcluster complex absorbing at 350 nm and emitting at 500 nm [4].

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Molecular Dynamics Simulation Study of the Microstructure of Ethylammonium Nitrate. The Effect of the Model Nitrate-Anion Geometry

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Ethylammonium nitrate (EAN) is a protic ionic liquid with a melting point of 287.6 K. EAN has been extensively studied in the recent years for both fundamental and technological reasons. Nevertheless, despite the considerable efforts, a detailed microscopic description of EAN structure on molecular level cannot be done on the basis of available data. In this case, molecular dynamics (MD) simulations, capable to provide a detailed molecular-level description of the structure of any liquid should be very fruitful for the further investigation of the issue. However, the major disadvantage of MD method is the sensitivity of simulation results to the model potentials employed.

The present study is focused on the effect of the model nitrate-anion geometry on the structure of anion local surrounding. Two different models of nitrate were considered. In the first case, anion was treated as flat 4-site group in which every atom was modelled by a single site (see Fig. 1). Partial charges and Lennard-Jones parameters were taken from Ref. [1]. In the second case, three virtual heavy sites with no charge were used to conserve anion mass and angular momentum, each one carrying one third of its total mass, while four massless atoms carried the partial charges and Lennard-Jones terms (see Fig. 2). The rest of the details is given in Ref. [2].

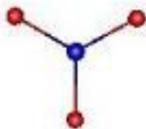


Fig. 1. 4-site model of NO_3^- anion.

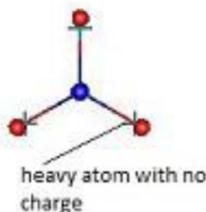


Fig.2 7-site model of NO_3^- anion.

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Interferometric Detection of the Electron g-Factor in Semiconductors

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The Lande factor, also known as g-factor, is a fundamental characteristic of the magnetic interactions in semiconductors and semiconductor nanostructures. Its distinction from the value given for the free electron, $g=2$, characterizes the spin-orbit interaction in bulk, the effective orbital movement of the electron, and the total angular momentum [1]. Applied to the quantum information processing, changing the g-factor in the vicinity of its zero value is of a particular interest. For example, Y. Kato *et al.* [2] suggested using this effect in order to address the single spin gates by electrical means controlling the sign of the g-factor. Therefore, developing of the structure with $g=0$ and precise measurement of the g-factor is a challenging problem. The second problem is addressed in this communication.

Following to Ref. 3, we use the interferometric setup (Fig. 1) for the determination of the light polarization change when the light beam passes through the investigated medium. We put the sample placed in a magnetic cryostat in a signal arm of the interferometer and analyze the Faraday rotation as function of the applied field. This allows us to extract the g-factor value with a very high degree of precision. In addition, we analyze advantages of the interferometric polarimetry compared to commonly used detection schemes.

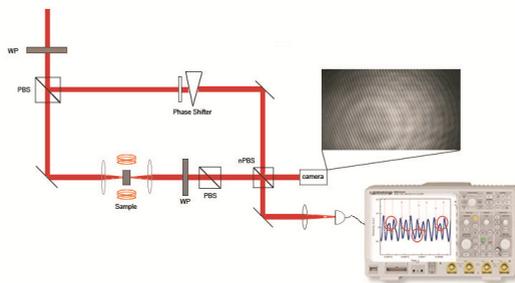


Fig. 1. The scheme of the interferometric setup.

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Implications of the Oxidative Stress for Structure and Stability of Second RNA-Recognition Motif of TDP-43 protein

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Reactive oxygen species (ROS) is a part of the chemical milieu of a healthy cell, widely employed as signaling mediators. However, an excessive level of ROS causes a systemic stress in the cell, interfering with essentially all of its vital functions. In the presence of reactive oxygen species, proteins with solvent-exposed cysteine side chains readily undergo disulfide-mediated dimerization (oligomerization). Disulfide bridges are fairly short linkages that bring into close contact protein surfaces which have not evolved to complement each other. The resulting random pairing of surface residues as occurs at the protein-protein interfaces is likely to have an appreciable destabilizing effect on the protein structure.

To test this hypothesis we have studied the effect of oxidative stress (modeled by hydrogen peroxide treatment) on the second RNA-recognition motif (RRM2) from the neuropathological protein TDP-43. ¹H-¹⁵N HSQC titration and H/D exchange experiments confirm that formation of disulfide-bonded dimers leads to a loss of protein stability. In addition, temperature-dependent ¹H spectroscopy indicates that dimeric RRM2 has lower melting temperature. As a negative control we have investigated the sample of RRM2 with C244S mutation, which does not form intermolecular disulfide bonds. The loss of structural stability caused by disulfide bonding under the conditions of oxidative stress may lead to increased proteolytic degradation of the RRM2 domain, resulting in formation of C-terminal fragments of TDP-43, which have been viewed as one of the causative factors in genesis of the neuronal inclusion bodies [1].

Acknowledgements. The study was supported by RSF grant 15-14-20038. Measurements were done using multiple facilities of research park of SPbSU.

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Loss of Protein Stability due to Formation of Intermolecular Disulfide Bonds under the Effect of Oxidative Stress: Case Study of the RRM2 Domain from Neuropathological Protein TDP-43

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In the presence of reactive oxygen species, proteins with solvent-exposed cysteine side chains readily undergo disulfide-mediated dimerization (oligomerization). Disulfide bridges are fairly short linkages that bring into close contact protein surfaces which have not evolved to complement each other. The resulting random pairing of surface residues as occurs at the protein-protein interfaces is likely to have an appreciable destabilizing effect on the protein structure. To test this hypothesis we have studied the effect of oxidative stress (modeled by hydrogen peroxide treatment) on the second RNA-recognition motif from the neuropathological protein TDP-43. ¹H-¹⁵N HSQC titration and H/D exchange experiments confirm that formation of disulfide-bonded dimers leads to a loss of protein stability. In addition, temperature-dependent ¹H spectroscopy indicates that dimeric RRM2 has lower melting temperature. As a negative control we have investigated the sample of RRM2 with C244S mutation, which does not form intermolecular disulfide bonds. The destabilizing effect of adventitious disulfide bridges has also been investigated by MD simulations of the RRM2 dimers. The simulations were conducted in explicit solvent under Amber 14SB force field; the data were used to predict HN solvent exchange protection factors, thus paving the way for comparison with the experimental results. The loss of structural stability caused by disulfide bonding under the conditions of oxidative stress may lead to increased proteolytic degradation of the RRM2 domain, resulting in formation of C-terminal fragments of TDP-43, which have been viewed as one of the causative factors in genesis of the neuronal inclusion bodies [1].

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Interpretation of ¹H and ¹³C NMR Spectra of Alizarin

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Alizarin may act as an antioxidant for the proteins under oxidative stress. This possibility has been suggested by our colleagues of University of Novi Pazar [1]. Thus, the research of this compound may detect these properties.

Method of Magnetic Resonance is very powerful tool of research molecular and atomic structure without destroying compound. That is why NMR spectroscopy is convenient for us. Solution of Red Alizarin in concentration 4,18% is used as sample, solvent is DMSO-d₆ with 99.8% deuterium atoms. The solution has been prepared and researched at the temperature of 25°C. NMR Spectra of it have been obtained with the Bruker 500 MHz Avance III spectrometer.

This data was analyzed using ACD/lab v12. The correlation of experimental lines with atoms of compound has been produced by ACD/lab Chemskech and ACD/lab Predictor. Theoretical calculation of the spectrum was performed in the author's program in the environment Matlab R2015b. It has helped to refine the values of the constants J-coupling and chemical shifts. The spectra and value of this constants will be discussed in the paper. This data will be used for research of possible chemical interactions between alizarin and oxidative stressed proteins, especially with oxidized low density lipoproteins (OxLDL).

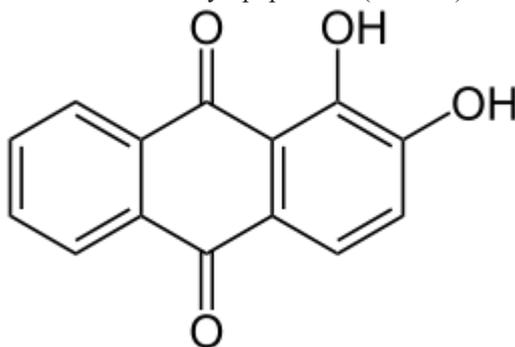


Fig. 1. Molecule of alizarin.

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Autocorrelation Analysis of ¹H NMR Spectra of RRM2 Domain of TDP-43 Protein Undergoing Temperature Denaturation

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TAR DNA-binding protein 43 (TDP-43) is 414-a.a.protein, which plays an important role in RNA control and transcription [1]. TDP-43 constitutes a major component of the inclusion bodies formed in the brains of the patients with frontotemporal lobar degeneration (FTLD) [2]. As it turns out, formation of CTF is a consequence of proteolytic cleavage within the RNA-recognition motif (RRM2) domain of TDP-43. RRM2 is a 65- residue globular domain with known structure (PDB ID 1WF0, 3D2W, 4BS2). Proteolytic cleavage within RRM2 leads to the loss of Nuclear Localization Signal located at the N-terminus of TDP-43 and exposure of Nuclear Export Sequence encoded in the RRM2. Consequently, TDP-25 are exported from nucleus into the cytoplasm, where they form the inclusion bodies. We hypothesize that proteolytic cleavage in RRM2 occurs as a result of a loss of structural stability caused by oxidative stress.

Our goal is to show that RRM2 structure can be destabilized under the conditions of oxidative stress by observing a reduction in the denaturation temperature of the protein. The oxidative stress would be simulated using hydrogen peroxide. In order to do that we have studied two samples: a control sample and an oxidized one. We have recorded ¹H NMR spectra at different temperatures.

To study the folding of RRM2 we have used the autocorrelation analysis of ¹H NMR spectra. The autocorrelation function is related to the dispersion of chemical shifts and carries the information about degree of foldedness of the protein and provides an effective method for examining the structural stability of the protein. This approach can be used to estimate the folding status of the protein [3]. As a result of such experiment we have observed the temperature denaturation of both control and oxidized samples. This experiment also showed that oxidizing RRM2 by hydrogen peroxide reduces its denaturation temperature by ca. 5 degrees.

Acknowledgements. The research was done using the equipment of the resource center “Center for magnetic resonance”, Research Park of SPbSU.

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Molecular Mobility of Ionic Liquid [BMIM]BF₄ in Silica Dispersions by Nuclear Magnetic Resonance

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Ionic Liquids (ILs) or molten salts as a class of compounds have aroused a burgeoning scientific interest in the past decades due to their useful properties for many present and potential industrial applications. In order to effectively use the ionic liquids in various technological applications it is necessary to study their molecular mobility. Transport properties are critical when the kinetics of synthesis reactions or ion transfer in an electrochemical device are considered.

The goal of this work was to determine transport properties of the ionic liquid [BMIM][BF₄] in the dispersion of Aerosil (SiO₂) by NMR method. For the study the samples consisting of three substances (Aerosil (SiO₂), deuterated acetonitrile (CD₃CN) and ionic liquid [BMIM][BF₄]) were prepared: **1** - [BMIM][BF₄] + CD₃CN + SiO₂, **2** - [BMIM][BF₄] + SiO₂, **3** - [BMIM][BF₄] + CD₃CN.

The presence of acetonitrile in the sample **1** causes a significant effect on the viscosity and this has an effect on the dynamics of [BF₄] in aerosil dispersion. To find out how acetonitrile increases the translational mobility of [BF₄] the temperature dependences of diffusion coefficients (*D*) have been investigated for all samples, using the pulsed magnetic field gradient NMR measurements (¹H, ²H and ¹⁹F) in the temperature range of 298 to 348 K. We also registered the dependences of *D* on the diffusion time in the range from 10 to 200 ms. Furthermore, the relaxation characteristics of ¹H, ²H and ¹⁹F nuclei were investigated in the temperature range of 298 - 348 K.

The dependences of diffusion coefficients and relaxation rates on temperature were used to determine the activation energies of the translational and rotational motions.

It was concluded that for the given object (aerosil) the self-diffusion coefficients weakly dependent on the interval (from 10 to 200 ms) between the gradient pulses. The effect can be explained by the shape of obstacles (in our case, the diffusion occurs between spheres). It was found that the presence of acetonitrile in the sample **1** significantly decreases the energy barrier for the translational motion reducing the viscosity of the system. Finally, the presence of acetonitrile decreases the values of relaxation rates in 2 times and increases the values of diffusion coefficients in 4 times.

Relaxation Efficiency of Gd and Fe Paramagnetic Ions in Aqueous Solutions of Fullerenols

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Currently, there is a wide range of methods for the study of human internal tissues. One of the most promising methods is the magnetic resonance imaging (MRI). To improve the accuracy of diagnostics by MRI so called “contrast agents” are used. As contrast agents, the endohedral metallofullerenes were suggested that was expected to increase the efficiency and sensitivity of the method [1].

In this work we investigated the aqueous solutions of fullerenols with Gd and Fe ions, placed inside the fullerene [2]. The investigated solutions were of different fullerene concentrations (0,1 mM/l; 0,5 mM/l; 1,0 mM/l; 2,0 mM/l; 3,0 mM/l; 4,0 mM/l; 6,0 mM/l; 8,0 mM/l; 10 mM/l) with different pH (3; 3.7; 7.8).

The measurements of concentration dependences of the T_1 and T_2 proton relaxation rates for two series of samples were carried out. The first series of samples contained the Fe (Fe^{2+} , Fe^{3+}) ions or endohedral metallofullerenes with Fe ions (with different pH), and the second one contained the Gd^{3+} ions or endohedral metallofullerenes with Gd ions (with different pH). The measurements were carried out at the proton resonance frequency of 20 and 90 MHz, at the constant temperature $T = 30^\circ\text{C}$.

Besides, the frequency dependences of relaxation rates for two solutions of endohedral metallofulleren with pH = 4 and two solutions with metal ions was studied at the resonance frequency of 300 and 500 MHz. For solutions with pH = 7 the temperature dependences were obtained in the temperature range 295 - 338° K at 500 MHz.

The peculiarities of the proton relaxation in the objects investigated are discussed.

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