Proceedings of the Japan-Russia Joint Symposium

«Chemical Theory for Complex Systems»,

September 19, 2014

St. Petersburg State University,
St. Petersburg, Russia

Organizers: Koichi Yamashita and Alexey Timoshkin

Scientific Program

Japan-Russia Joint-Symposium on Chemical Theory for Complex Systems

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Organizers: Koichi Yamashita and Alexey Timoshkin

8.30 – 9.00 Poster mounting

9.00 – 9.10 Opening of the symposium. **Alexey Timoshkin**

9.10 – 10.50 Oral presentations. Chair: **Alexey Timoshkin**

9.10-9.35 **O-1. Keiji Morokuma**, Kyoto University
"Theory and Computation Provide Insights and Discovery on Chemical Reactions of Complex Molecular Systems"

9.35-10.00 **O-2. Andrei Zaitsevskii**, Moskow State University
“Chemical bonding in transuranium element higher oxide molecules"

10.00-10.25 **O-3**. **Shigeyoshi Sakaki**, Kyoto University
"Reaction behavior of transition metal complexes with unusual valence"

10.25-10.50 **O-4. Vladimir Sizov**, St. Petersburg State University.
“Conducting polymers based on transition metal complexes with Schiff bases: bringing together experiment and calculations”

10.50 - 11.10 Coffee break and poster viewing.

11.10 – 12.25 Oral presentations. Chair: **Shigeyoshi Sakaki**

11.10-11.35 **O-5**. **Anatoly Titov**, St. Petersburg Nuclear Physics Institute
"Efficiency of relativistic pseudopotentials and DFT methods to study chemistry of actinide and transactinide elements".

11.35-12.00 **O-6**. **Koichi Yamashita**, University of Tokyo
"A Reparametrization Approach of DFT Functionals Based on the Equilibrium Temperature of Spin Crossover Compounds"

12.00-12.25 **O-7. Anna Pomogaeva**, St. Petersburg State University.
“The effect of terminal groups on electronic properties of group 13-15 nanoneedles”.

12.25 – 14.00 Lunch

14.00–15.40 Oral presentations. Chair: **Koichi Yamashita**

14.00-14.25 **O-8. Aleksandr Tulub**, St. Petersburg State University.
"On the stability of magnetic properties of FeSi(n) clusters (n=4-12) by high temperature in a framework of MCSCF method".

14.25-14.50 **O-9**. **Kazuo Kitaura**, Kobe University
"Recent development of the fragment molecular orbital method"

14.50-15.15 **O-10. Alexey Timoshkin** St. Petersburg State University.
"Lewis Superacids and Donor-Acceptor Cryptands: From Noble Gas Complexes to Hydrogen Splitting".

15.15-15.40 **O-11. Jun-ya Hasegawa**, Hokkaido University
"Excitation energy transfer pathways in bridged donor-acceptor systems"

15.40-16.00 Coffee break and poster viewing.

16.00-16.50 Oral presentations. Chair: **Anna Pomogaeva**

16.00-16.25 **O-12**. **Masataka Nagaoka**, Nagoya University
"Toward Controlling Complex Chemical Reactions in the Molecular Aggregation States-From Multiscale Simulation to Computational Molecular Technology"

16.25-16.50 **O-13. Alexander Khlebnikov**, St. Petersburg State University.
How DFT calculations can help to synthetic organic chemist.

16.50-17.50 Poster viewing and discussions.

P-1. **Yuri Demidov**, St. Petersburg Nuclear Physics Institute
Ab-initio simulation of element 113 hydroxide molecular structure and properties

P-2. **Christina Reshetova**, St. Petersburg State University.
"Spectroscopic and quantum-chemical investigations of chloro- and nitro-bis-bipyridyl complexes of ruthenium(II) with 4-substituted pyridine ligands"

P-3. **Anna Lisovenko**, St. Petersburg State University.
Influence of donor-acceptor interaction on hydrogenation of borazine and polyborazines

P-4. **Dmitri Doinikov**, St. Petersburg State University.
Requirement of Grimme's dispertion correction for DFT calculations of B–N complexes.

P-5. **Ilya Kopanichuk**, St. Petersburg State University.
Adsorption of Lennard-Jones fluid in finite slit-shaped pores

P-6. **Anastasia Sizova**, St. Petersburg State University.
Computer simulation of CO_2/CH_4 mixture adsorption in porous materials: effects of pre-adsorbed water

P-7. **Maria Novozhilova**, St. Petersburg State University.
Spectroelectrochemical Studies of Electrodes Modified by Polymer Complexes of Nickel with Schiff Bases

P-8. **Pavel Snegurov**, St. Petersburg State University.
Molecular dynamics simulation of ionic conductivity in yttria-stabilized zirconia.

17.50-18.00 Closing of the symposium. Prof. **Keiji Morokuma**.

ORAL PRESENTATIONS

Poster presentations:

ORAL PRESENTATIONS

O-1. Keiji Morokuma, Kyoto University

Theory and Computation Provide Insights and Discovery on Chemical Reactions of Complex Molecular Systems

Keiji Morokuma

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The chemical reaction that creates, destroys, reorganizes chemical bonds to produce new compounds is the most important subject of chemistry. Theoretical/computational studies have come a long way and are now playing the central role in providing insights in understanding the mechanism and dynamics of chemical reactions as well as in discovery of new reaction mechanisms and reaction systems. The theory can study not only the reaction of the ground state of molecules in gas phase but also reactions of excited electronic states as well complicated reactions of complex molecular systems. The information theoretical/computational studies can provide is often complementary to the information experimental studies provide, and research on chemical reactions is becoming impossible without strong collaboration between theorists and experimentalists.

In the present talk, I will discuss some of our recent studies of chemical reactions. We have developed the Global Reaction Route Mapping (GRRM) strategy for automatic exploration of reaction pathways of complex molecular systems. The ADDF (anharmonic downward distortion following) and the AFIR (artificial force induced reaction) methods in the GRRM strategy have been used for determination of not only energy minima and saddle points on the potential energy hypersurfaces but also minima and saddle points on the conical intersection and crossing seam hypersurfaces. I will discuss the GRRM strategy and applications to several reaction systems, including photodissociation reactions, catalytic reactions and enzymatic reactions.

Discussion:

A. Y. Timoshkin: When you study reactions in solution, do you take the solvent into account as a molecule or as a medium force?

K. Morokuma: Typically we put 6, 7, 8 solvent molecules and we try to fill the first solvation shell. As soon as the next molecule goes into the second solvation shell, we assume that that can be handled by the continuum model. So we try to include as many solvent molecules in the first solvation shell, those will react. But I have found that molecules from the second solvation shell can come and react sometimes, so one have to pay attention.

A. Y. Timoshkin: The second question is about artificial force you apply. You showed examples where you applied the force and nothing happened. So, how do you know where to apply artificial force?

K. Morokuma: To me, one should take forces between any pairs of atoms in the big molecule, but this is very expensive. Therefore, we apply artificial force selectively. This is bias a little bit. But when we put forces, we do not make assumptions about TS. Sometimes if you put the wrong force, it does not react, then we apply it somewhere else. And the amount of the force is also very important. It the force is too strong, then very dominant path sucks everything in, you miss less popular, smaller pathways (with small barriers). If force is too small, you have caught by barrier, so AFIR is very delicate method.

O-2. Andrey Zaitsevskii, Moscow State University

CHEMICAL BONDING IN TRANSURANIUM ELEMENT HIGHER OXIDE MOLECULES

A. Zaitsevskii[a,b], L.V. Skripnikov[a,c], W.H.E. Schwarz[d], A.V. Titov[a,c]

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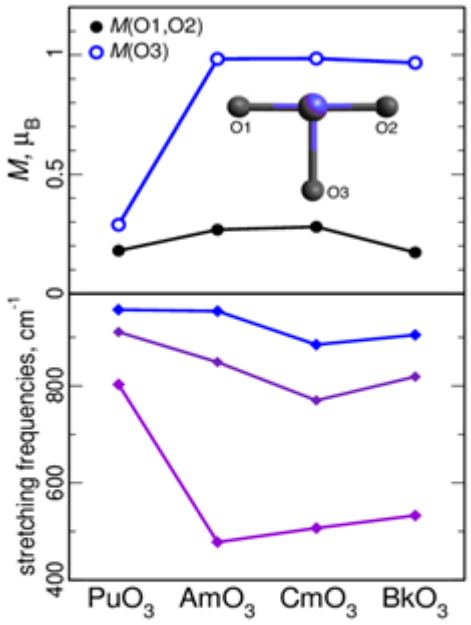
Modern accurate small-core relativistic pseudopotential models [1] combined with the two-component non-collinear density functional theory (2c DFT, [2]) offer a possibility to quantitatively describe chemical bonding in transuranium element compounds ([3] and references therein). Due to a rather low cost of calculations, this approach can be directly applied to systems composed of dozens and hundreds of atoms. To facilitate the analysis of chemical behavior of more complex systems by invoking chemical expertise and intuition, it is desirable to translate the results of the direct electronic structure modeling into conventional chemical terms such as valence, oxidation state, bond order, effective state of an atom or a group in a compound etc. This task is not simple, because DFT calculations in principle should not yield approximate wavefunctions or density matrices required to get bond orders and atomic orbital occupancies through natural bond orbital or Mayer analysis. Although the Kohn-Sham wavefunction of the non-interacting electron system is frequently used as a source of information on atomic orbital occupancies and bond orders in the corresponding real system,

the application of this stratagem to complicated bonding pictures in poorly studied compounds seems somewhat risky. At the same time, built-in 2c-DFT entities, i.e. total electronic energy as a function of nuclear coordinates (energy minima positions, force constants or vibrational frequencies) and charge and magnetization density distributions provide enough information to consistently determine oxidation states and bond orders in difficult cases such as that of the compounds of transuranium elements in higher oxidation states.



Absolute values of magnetization densities integrated over Bader basins of oxygen atoms (M) and stretching vibrational frequencies for AnO_3 molecules, An = Pu through Bk

For example, a simple analysis of absolute values of spin magnetization densities integrated over the Bader atomic domains, M (≈ effective number of unpaired electrons localized on the corresponding atoms) and stretching frequencies of T-shaped Pu, Am, Cm and Bk trioxide molecules (see the figure) provides valuable information on the bonding nature. Small M values for all oxygen atoms and three high stretching frequencies are compatible with the model of three O^{2-} ions doubly bonded to Pu and the plutonium oxidation state +6. In other trioxides, M values correspond to single unpaired electron on one of the oxygen atoms (O3), and the lower frequencies which become fully localized on An-O3 stretching mode correspond to single An-O3 bonds, the formal charge −1 on O3, and the actinide oxidation state +5. This result agrees with the conclusion drawn from the studies of An•4O species in [3]: the ability to reach high oxidation states in oxygen compounds should decrease in passing from Pu to later actinides.

Effective state of a heavy atom in a compound which can be derived through the analysis of most experimental data (X-ray and Mössbauer spectroscopy, NQR, etc.) is mainly determined by the behavior of the valence / subvalence part of the wavefunction in the vicinity of the nucleus. If one uses the pseudopotential model, this behavior is in turn related to that of the pseudo-wavefunction in the same region [4]. Note that the Kohn-Sham one-electron

functions and one-electron density matrix get some physical sense near the nuclei where the strong external field dominates over correlations. Thus, it is logical to define an "atom-in-compound effective configuration" within the 2c-DFT as a set of fractional occupancies of atomic spinors which yields valence / subvalence atomic Kohn-Sham density matrix fitting (in some averaged manner) the molecular Kohn-Sham density matrix near the nucleus of the considered atom. The dependence of the resulting configurations on the oxidation state of actinide atoms in oxides has been studied. The sums of occupancies agree reasonably with the Bader atomic charges. The effective configuration can differ significantly from the formal one; for instance, the *f*-shell occupancies in the PuO_n, molecules, n=1–4 (plutonium oxidation states close to +2n confirmed by M(O) and frequency analysis) grow with n much slower than their formal counterparts.

We thank Prof. C. van Wüllen for supplying us with his 2c DFT code [2]. The work was supported by the Russian foundation for Basic Research (grant # 13-03-01234a).

[1] N.S. Mosyagin, A. Zaitsevskii, A.V. Titov, *Int. Rev. At. Mol. Phys.* **1**, 63 (2010)

[2] C. van Wüllen, *Z. Phys. Chem.* **224**, 413 (2010)

[3] A. Zaitsevskii, W.H.E. Schwarz, *Phys. Chem. Chem. Phys*. **16**, 8997 (2014)

[4] A.V. Titov, Yu.V. Lomachuk, L.V. Skripnikov, submitted to *Phys. Rev. A* (2014)

Discussion:

A. V. Tulub: Did you calculate hyperfine interaction? Do you have some experimental evidence?

A. Zaitsevskii: I have no experimental hyperfine data, but it will be very simple to pass to the solid state to take large clusters and to perform the experiment. The partial charges and effective occupancies we have should correlate with them, we will see.

P. A. Snegurov: You showed periodic table with Ir(VIII). Where I can find information about it? Do you think it is real Ir(VIII)?

A. Zaitsevskii: There is metastable oxide IrO_4. It can exist relatively long time at cold conditions, you can simply google or get a reference from my paper. It is symmetrical molecule with four Ir=O bonds, so it is really Ir(VIII) at low temperatures. It was registered by a large number of experimental techniques, but the substance is not stable. If we find in future PuO_4, it will also exist only at low temperatures.

O-3. Shigeyoshi Sakaki, Kyoto University

Catalytic Reactions by Transition Metal Complexes with Unusual Valence. Theoretical Study

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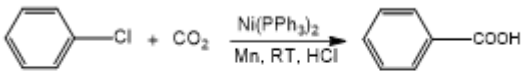
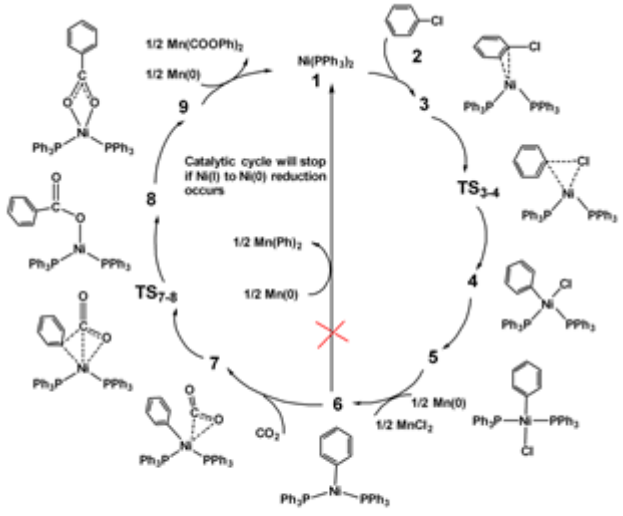
Organometallic reactions and catalytic reactions by transition metal complexes are important research target in theoretical and computational chemistry, because theoretical knowledge of reaction mechanism and reaction features such as energy change, geometry of transition state and key intermediates are indispensable for well understanding of catalytic reaction and new advancement of the catalytic chemistry of transition metal complexes. In my understanding, two new trends are found in organometallic chemistry; one is to use heavy main group element for activation of small molecule and catalytic reaction. The other is to use unusual valence in the catalytic cycle. To achieve successful advancements in these two trends, theoretical and computational knowledge is indispensable.

Recently, we theoretically investigated what are characteristic features in heavy main group element species and found how to construct the catalytic cycle.[1] However, theoretical study has been limited for unusual valence in catalytic reaction. Several interesting and pioneering works are reported in experimental field. Ni-catalyzed carboxylations of phenyl chloride and benzyl chloride with carbon dioxide suggest that a Ni(I) species plays a crucial role in the catalytic reaction (Scheme 1),[2] despite that many catalytic reactions by group 10 transition metal complexes occur via M(0)/M(II) catalytic cycle. Also, benzene synthesis catalyzed by dinuclear Mo complex suggests that the Mo-Mo quintuple bond plays a crucial role;[3] remember that the valence of the metal in M-M multiple bond is very different from that of usual mononuclear metal center.[4] We theoretically investigated these reactions to clarify the important role of unusual valence in the catalytic reaction.



Scheme 1. Carboxylation of phenyl chloride

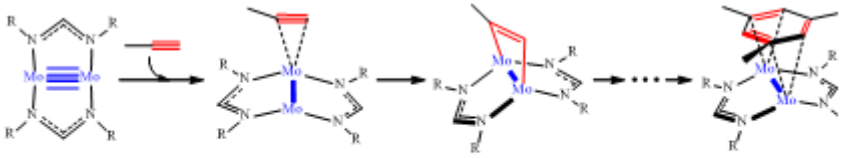
In the nickel-catalyzed carboxylation of phenyl chloride with carbon dioxide, the first step



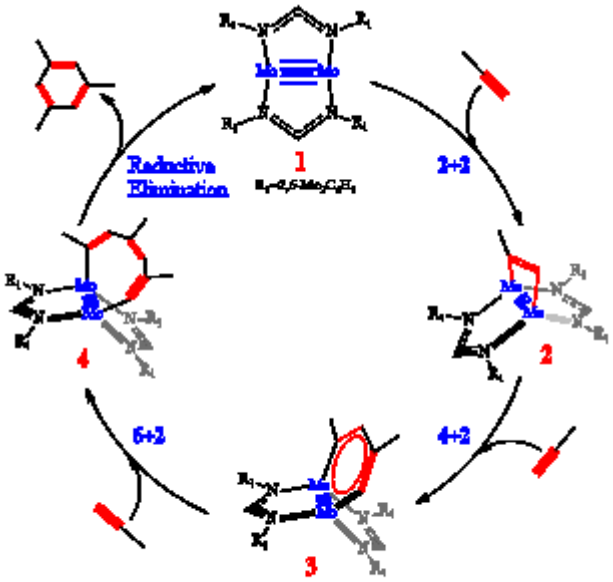
Scheme 2. Catalytic Cycle of Ni-catalyzed carboxylation of phenylchloride

is the oxidative addition of phenyl chloride to $Ni(PPh_3)_2$ to afford $NiCl(Ph)(PPh_3)_2$, as expected.[5] The second step is not CO_2 insertion into the Ni(II)-Ph bond. This insertion is very difficult. However, $NiCl(Ph)(PPh_3)_2$ undergoes one-electron reduction with Mn powder to form a nickel(I) species. The nickel(I) species is very reactive for CO_2 insertion. This is because the charge-transfer from the Ni-Ph moiety to CO_2 significantly occurs in the insertion into the Ni(I)-Ph bond: The importance of the CT was discussed previously[6]. Based on the results, the strong point of the first-row transition metal complex is discussed here.

In the catalytic synthesis of benzene by a Mo dinuclear complex, one acetylene reacts with a Mo-Mo quintuple bond to afford a four-member metallacyclic compound with a Mo-Mo quadruple bond.[7] After that, the second and third acetylenes are inserted into the Mo-C bond. The first step seems We elucidated that characteristic MOs of Mo-Mo quintuple bond play important symmetry-forbidden 2+2 coupling reaction in a formal sense. But, the reaction occurs via an asymmetrical reaction course to avoid such symmetry forbidden character (Scheme 3).



Scheme 3. Benzene synthesis by Mo-Mo quintuple bond



Scheme 4. Catalytic cycle of benzene synthesis

The second and third steps are considered to be an alkyne insertion into the Mo-C bond. The last is the reductive elimination. The rate-determining step is the third step in which eight-member ring including two Mo atoms is formed. In all these elementary steps, the $d\delta$-$d\delta$ bonding orbital of the Mo-Mo quintuple bond plays a crucial roles. It is the origin of this catalytic reaction. Thie importance of $d\delta$-$d\delta$ MO of the metal-metal multiple bond is newly found in this work.

References

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[6] (a) Sakaki, S.; Kitaura, K.; Morokuma, K. *Inorg. Chem.* **1982**, *21*, 760. (b) Sakaki, S.; Kitaura, K.; Morokuma, K.; Ohkubo, K. *Inorg. Chem.* **1983**, *22*, 104.
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Discussion:

A. V. Tulub: My question is about the experimental evidence [of the existence of intermediates]: how it can be done? in solution?

S. Sakaki: This reaction was carried out in solution. One intermediate compound was isolated and structure was analyzed by X-ray. The experimental structure is essentially the same as optimized structure (structural parameters different). Other intermediates have not been isolated.

O-4. Vladimir Sizov, St. Petersburg State University.

Conducting polymers based on transition metal complexes with Schiff bases: Bringing together experiment and calculations

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In recent years conducting polymers are being increasingly used in a variety of applications such as supercapacitors, solar cells, and electroluminescent devices. An important class of these compounds is represented by polymers based on transition metal complexes. Conducting coordination polymers present a major challenge for computational chemistry because the molecular-level basis of their electrochemical performance has not yet been investigated in detail.

The goal of the present work is to develop and implement a multiscale computational approach to the structure-property relationships in conducting polymers formed from [MSchiff] transition metal complexes with SalEn-type Schiff-base ligands. This approach is comprised of four blocks, which are intended to resolve specific problems related to the synthesis, stability, and performance of the polymers under investigation:

Quantum chemical study of [MSchiff]n monomers and oligomers	Effects of metal atom and substituents on the structural, spectral and electrochemical properties of polymers. Possible mechanisms of charge transfer in polymers.
Quantum chemical study of oxidized forms of [MSchiff]n complexes with various axial ligands (see Fig. 1)	Analysis of electronic structure and bonding in complexes with coordinated solvent or other molecules. Potential applications of poly-[MSchiff] in electrochemical sensors.
Quantum chemical study of stacks comprised of several [MSchiff]n molecules	Investigation of cross-linking between polymer chains.
Molecular dynamics study of [MSchiff] complexes in solution	Aggregation of complexes prior to polymerization. Solvation shell structure and possible mechanism of hydrolysis.

Computational studies of metal-SalEn complexes using density functional theory (DFT) provide a good description of the electronic structure of these compounds and their spectroelectrochemical properties [1]. However, an accurate description of the changes of electronic structure upon oxidation of the complexes requires explicit treatment of coordinated solvent molecules (e.g., acetonitrile).

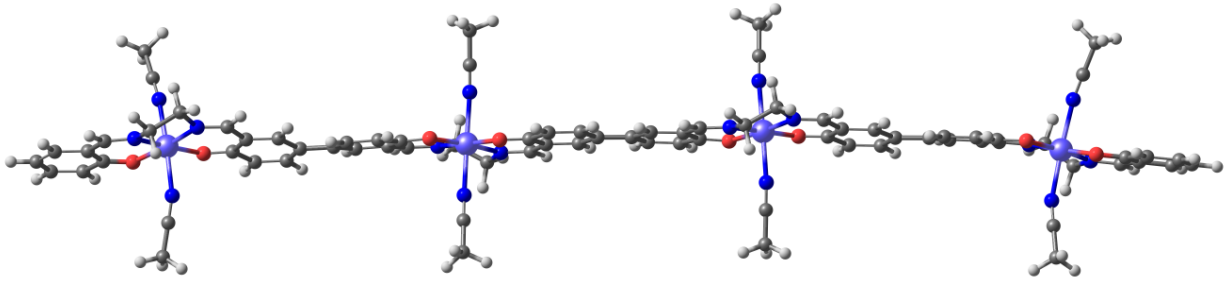

Figure 1. Oxidized [NiSalEn]4^{4+} complex with eight coordinated acetonitrile molecules

Without coordinated solvent the process of $[MSchiff]_n$ oxidation is predominantly ligand-centered, while in the presence of axial ligands it is metal-centered due to the stabilization of higher oxidation states of the metal. According to the results of DFT calculations, intermediate oxidized forms may be both metal-centered or delocalized, which is in agreement with experimental observations of different charge-transfer mechanisms in poly-[NiSchiff] films.

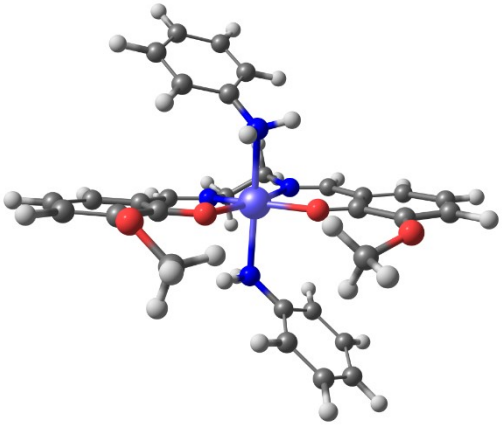

Figure 2. [Ni(CH3O)2SalEn]$^+$ complex with two aniline molecules

DFT computational study of oxidized $[NiSchiff]^+$ monomers with various axial ligands revealed several possibilities for coordination of organic molecules to the complex. Coordination to the metal atom (Fig. 2) typically results in stabilization of the oxidized form of the metal (e.g., Ni^{III} for nickel), while formation of single or multiple H-bonds with oxygen atoms favors ligand-based oxidation and facilitates charge transfer from coordinated molecules to the complex. The results of DFT calculations show a reasonable correlation with the experimental data on the electrochemical response of poly-[NiSchiff] films in the presence of various additives.

The quantum chemical treatment of stacking interactions between short fragments of polymer chains indicates that cross-interactions might play an important role for oxidized

polymers. The exact nature of these interactions has yet to be studied in detail, though preliminary data suggest *d*-*d* or π-π stacking rather than *d*-π.

Finally, molecular dynamics simulations can provide a molecular-level insight into the behavior of [MSchiff] complexes in solution, revealing the possibilities for aggregation of monomers and elucidating the role of various factors (e.g., nature of background electrolyte or properties of electrode surface) on the structure of poly-[MSchiff] films.

[1] V.V.Sizov et al. J.Solid State Electrochem. (2014): DOI 10.1007/s10008-014-2619-4.

Discussion:

S. Sakaki: You mentioned Ni(III) complex which coordinates acetonitrile, how you determine the oxidation state of the Ni center?

V. V. Sizov: The problem of determining the oxidation state of Ni is really a problem. We started from orbital populations, but after series of computations for test compounds which are normally known as Ni(II) and Ni(III) complexes we actually did not see the difference. Our primary instrument for determining oxidation state of Ni is spin density.

S. Sakaki: Did you find spin density on Ni center?

V. V. Sizov: Yes, we have spin densities.

S. Sakaki: The second question is about very interesting Ni(II)-Ni(III) bridged system. For this compound you found unknown absorption peak.

V. V. Sizov: No, for the mixed valence compound the spectrum looks quite OK. The problem arises with the fully oxidized form, which is Ni(III)-Ni(III). My guess is that this form is not observed in experimental studies because the delocalized form is lower in energy. I would say that it should not have this band, but should have absorption around 500 nm. I do not have the firm proof of this hypothesis, but that is our current opinion on this problem.

S. Sakaki: I think that we have Ni(III) – Ni(II) intervalence absorption in the studied range. Do you think that this unknown peak corresponds to intervalence transition?

V. V. Sizov: I would say (it is my guess based on former experience) that it may be metal to ligand charge transfer. In fact, the metal to metal charge transfer (MMCT) is not a very strong factor influencing the spectrum. We see MMCT components at certain bands but I would say that there is no single band that is primarily influenced by MMCT.

O-5. Anatoly Titov, St. Petersburg Nuclear Physics Institute

EFFICIENCY OF RELATIVISTIC PSEUDOPOTENTIALS AND DFT METHODS TO STUDY CHEMISTRY OF ACTINIDE AND TRANSACTINIDE ELEMENTS

A.V. Titov[a,d], A.V. Zaitsevskii[b,c], N.S. Mosyagin[b,d], A.N. Petrov[b,d], L.V. Skripnikov[b,d], Yu.A. Demidov[b]

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Our latest advances in studies of actinide and superheavy element (SHE) chemistry using the shape-consistent two-component small-core relativistic pseudopotential (RPP) method and two-component relativistic density functional theory (2c–RDFT) are summarized. The features of these elements due to large relativistic effects are emphasized. The RPP model leaving for explicit correlation treatment both valence and subvalence (outercore) electrons accounts for the finite nuclear size and incorporates relativistic effects (including the bulk of Breit interactions), providing a good basis for attaining optimal accuracy/cost ratio in the cases of large and strongly interfering relativistic and correlation effects characteristic for the heavy element compounds. The RPP/2c–RDFT approach allows one to solve the outercore-valence many-electron problem with moderate computational expenses while using practically exhaustive basis sets optimized for the case of large differences between ***nl(j=l+1/2)*** and ***nl(j=l-1/2)*** one-electron states.

Because of the exceptional role of thermochromatography on gold in the experiments on the "chemical" identification of SHE with atomic numbers $Z \geq 112$, main attention was paid to the description of the SHE – gold-cluster interactions. Adsorption energies of SHE on gold surface were estimated using the cluster model (see Figs. 1, 2). Its reliability was improved by

monitoring the charge distributions in the vicinity of the adsorption site taking into account the effects of relaxation of the cluster compatible with its embedding into the crystal. In some cases the results differ significantly from those of previous theoretical studies. For instance, new estimates of E113/Au and E120/Au adsorption energies (1.0–1.2 eV and 2.5–2.7 eV, respectively) are recommended.

Fig 1: Cluster models of adsorption complexes of **SHE atoms** on metal surfaces (mainly Au).

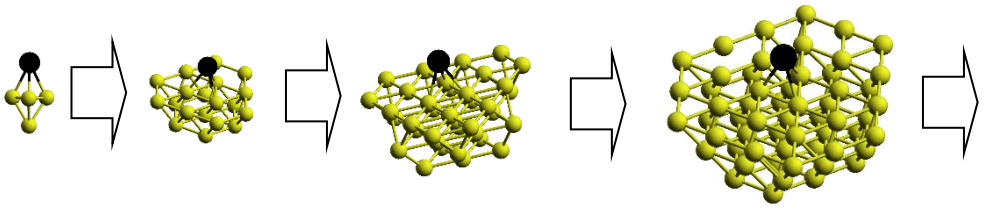
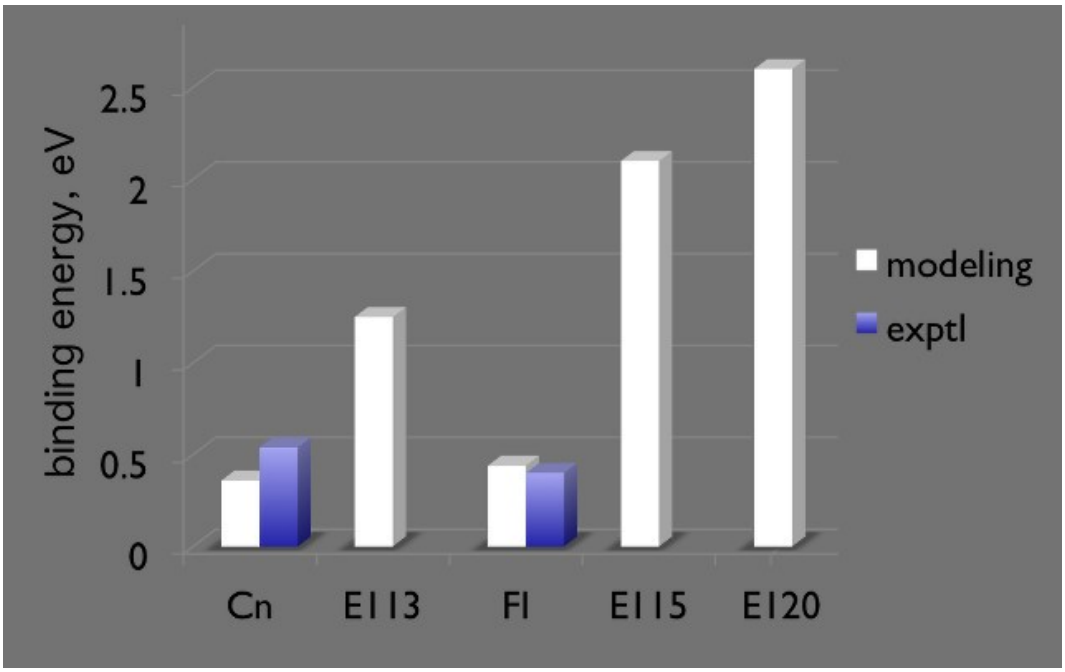


Fig.2. Binding energies of single SHE atoms on Au surface according to RPP/2c–RDFT modeling and experiment. 2c–DFT should underestimate Cn/Au binding energy by 0.1-0.2 eV, no reasons to expect similar systematic errors in other cases.



We also report calculations of Cn–Au_n and E113–Au_n complexes (for small n) by a hybrid scheme combining *ab initio* scalar–relativistic correlation calculations with the estimation of spin-dependent relativistic effects (effective spin-orbit couplings) through geometry–dependent corrections to interaction energies obtained at the 2c–RDFT level. The necessary accuracy of

the correlation treatment is ensured by the use of an accurate coupled–cluster technique and the extrapolation to the complete basis set limit. We have to stress that our scheme does not imply the smallness of spin–dependent interactions or the neglect of their interference with electron correlations.

The work was partially supported by the RFBR (grants Nos. 13-03-01307, 13-03-01234, and 13-03-12252-ofi_m-2013). Thanks are to Prof. C. van Wüllen for supplying us with his 2c–RDFT code. The calculations were performed at MCC NRC "Kurchatov Institute" (http://computing.kiae.ru/).

Discussion:

J-Y. Hasegava: I have a question about importance of spin-orbit interactions. Spin-orbit interactions should be very small compared to perturbation. Is it right approach to use for general cases or only for special cases?

A V. Titov: It should not change the electronic structure, it should not perturb the wavefunction, but it can be large. It depends on the case. In general, it is possible but you should be careful to treat spin-orbit coupling.

J-Y. Hasegava: Another question is how pseudopotential affects chemical properties.

A V. Titov: For the normal cases it is not important, even for heavy atoms; it is important only in case of quasi-degeneration. For example, for the element 112 (Cn) the difference in two electronic levels is only 0.2 eV. It also may be important for f-elements (f shell is deep lying). It is more important if you need to treat the ground and excited states.

S. Sakaki: You mentioned interference between London interactions and relativistic effects. How one can understand the influence of pseudopotential to valence London interactions?

A V. Titov: This interference is not well studied. Because in the case of gold, nobody says about London interactions, people say its aurophilic interactions. But in order to find what is aurophilic interaction it is reasonable to suggest the interference with London interactions. However, in some situation it is more complicated (both chemical contribution and quantum contribution of the high order.

O-6. Koichi Yamashita, University of Tokyo

Computational Materials Science for Energy Conversion

Koichi YAMASHITA*[1]*

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[A] A re-parametrization approach of the DFT functionals based on the equilibrium temperature of the spin crossover compounds [1]

In order to study the electronic properties of the spin crossover compounds an approach providing a reliable estimate of HS/LS energy gaps while retaining an accurate and efficient method for computing the ground state energy is required. We investigate the energy splitting between the high-spin state and the low-spin state of $Fe(btr)_2(NCS)_2.H_2O$ spin crossover single molecule using different DFT functionals. The derived results exhibit a large deviation and several methods mis-estimate the HS/LS energy gap. Such fact stirs the need for a valid criterion leading to a reliable estimation of the HS/LS energy gap. A re-parametrization approach of the DFT functionals based on the equilibrium temperature of the spin crossover compound is proposed. Based on such approach, the different calculation methods converge to comparable HS/LS energy gaps.

[B] DFT Analysis on the Electronic Properties of Methylammonium Lead Iodide Perovskite[2]

Methylammonium (MA) lead iodide perovskite ($CH_3NH_3PbI_3$) plays an important role in light absorption and carrier transport in efficient organic−inorganic perovskite solar cells. In our poster, the theoretical estimation of effective masses of photocarriers and the role of MA cation in $CH_3NH_3PbI_3$ will be discussed. Spin-polarized DFT calculations have been performed with the GGA. From the charge density of the two-fold degenerate states of CBM and those of VBM, one can see that photogenerated electrons around CBM and holes around VBM exist separately, results related to the ambipolar transport nature of the material. Effective masses of photogenerated electrons and holes are estimated to be $m_e^* = 0.23m_0$ and $m_h^* = 0.29m_0$, respectively, including spin−orbit coupling effects. This result is consistent with the long-range ambipolar transport property and with the larger diffusion constant for electrons compared with that for holes in the perovskite, which enable efficient photovoltaic conversion.

We also focus our attention on the MA cation and studied the role it plays in the electronic/optical features of the perovskite.

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Discussion:

A. V. Pomogaeva: I have a question about the first part of your presentation to treat spin crossover systems. Did I understand correctly that parametrization is applicable to treat only these particular systems? Are there ways to make it universal?

K. Yamashita: For these systems, it works, but to generalize it is very difficult.

A. V. Pomogaeva: For the second part of your presentation, which software did you use for the optimization?

K. Yamashita: We used WASP.

K. Morokuma: You are used optimization for crystals of for molecules [for the first part of the presentation]?

K. Yamashita: We have done optimization for molecules. They are not so different, we expect.

O-7. Anna Pomogaeva, St. Petersburg State University.

The Effect of Terminal Groups on Electronic Properties of Group 13-15 Nanoneedles

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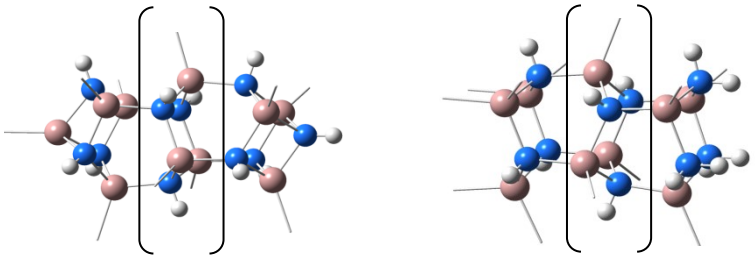
Abstract. Theoretical investigation of structural and electronic properties is presented for the imido rods $[RMNH]_{3n}$ (M=Al, Ga,In; R=CH_3,H) with different types of terminal groups. Electronic structures of the oligomers were studied at DFT and TDDFT level of theory. Rods up to 10 nm of length were considered. Band structure of the infinite polymer was build. A type of terminal groups of the oligomers is found to have a dominant influence on their electronic properties.

1. INTRODUCTION

GaN based materials are known to be semiconductors of high temperature and chemical stability and high electron mobility which made them attractive for a variety of applications. Bulk GaN is a source of light emission in the ultraviolet region. Doping with inclusions, for example with In, can shift the emission into a visible blue region. On the other hand, for nanosized materials varying of particles' size and shape is another level of controlling electronic properties of the material to tune them for a particular application.

The present study is devoted to theoretical investigation of structural and electronic properties of rod-like molecular clusters formed by stocking of cyclotrigallazane rings $[RGaNH]_3$ (R=CH_3,H) stability of which was predicted [1] and a family of such compounds were synthesized [2]. These compounds are potential candidates for molecular engineering. There are two types of ending of the oligomers. Schematically they are shown in the Figures 1. So-called "closed" oligomers are capped by additional metal-radical and imido groups. The other type is so-called "open" oligomer where the dangling bonds on the edges are simply saturated by hydrogens or functional groups.

In this research we considered how electronic properties of the open and closed forms of $[RMNH]_{3n}$ nanorods could change upon variations in size, shape and compositions. For small sized clusters (n=3) we considered substitutions of Ga atoms by Al or In elements. We studied a change in properties by varying functional groups considering hydric and alkyl forms of the rods. And finally, we investigated the impact of chains' elongation up to 10 nm of length.



(a) (b)

FIGURE 1. Schematic representation of closed MR-$[MRNH]_{3n}$-NH (a) and open R_3-$[MRNH]_{3n}$-H_3 (b) structures. Pink color refers to metal atom's sites, NH groups are represented by blue and gray, and R=CH_3/ H sites are presented by open bonds.

2. COMPUTATIONAL METHOD

All structures were fully optimized at DFT B3LYP/SVP level, reliability of which was proven earlier [3]. Absorption spectra of $[CH_3MNH]_9$ (M=Al, Ga, In) were obtained via TDDFT/TZVP calculations. Band structure of the polymer $[HGaNH]_{3n}$ (n->∞) was built from B3LYP/SVP oligomer (n=38) calculation using projection method [4]. All quantum chemical computations were performed in Gaussian 09.

3. RESULTS AND DISCUSSION

3.1 Molecular Structures

The common feature of the relaxed geometry of all considered rods that metal-nitrogen interring bond lengths are longer in the middle and shorter at the ends, while in-ring bond lengths are shorter in the middle and longer at the ends. The most significant is a difference in bond lengths distribution along a rod between closed and open structures.

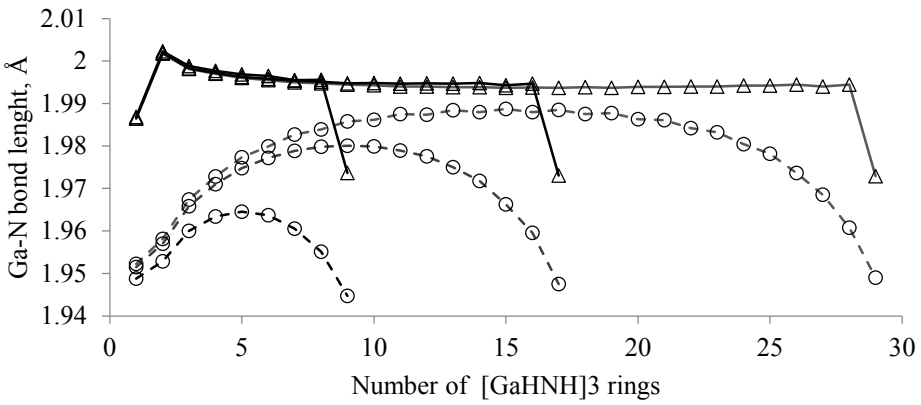


FIGURE 2. Interring Ga-N bond lengths for relaxed closed (triangles) and open (circuls) $[HGaNH]_{3n}$ rods with n=10, 18 and 30. Lines are drawn to follow eye.

In the Figure 2 interring B-N bond lengths are presented for open and closed $[HGaNH]_{3n}$ oligomers with n=10,18 and 30 as distributed along the chains. Bond lengths at the very edges of the closed chains are significantly shorter than those in the middle. However, all other bonds are nearly equal to each other demonstrating a well periodicity. Bond lengths of the open chains are smoothly distributed along the rods remaining shorter than the ones in closed structures even for the longest chain.

3.2 Electronic Structures

All the considered molecules are polarized with a dipole moment vectors directed from heavier atom caped ends to nitrogen caped ends. However, the values of the dipole moments of open clusters are much larger (14.4 D vs. 1.8 D for open and closed $[CH_3GaNH]_9$ rods respectively) and faster increasing with the length of the rod. HOMO and LUMO states of open clusters and heavily localized at the different ends of the rod that can cause a charge transfer upon excitation. The energy gaps of open rods are significantly smaller than the gap the closed cluster of the same size and rings' composition.

Al/In Substitutions

Substitution Ga atom by Al leads to moderate monotonous increasing of energy gaps with dopant concentration for both open and closed rods. Substitution of Ga atoms by In not only causes a significant reduction in the value of energy gap but also depends on the position of the substituted atom in the oligomer related to the rod's ends.

Calculated absorption spectra for $[CH_3MNH]_9$ reveal a rad shift from M=Al to M=Ga and from M=Ga to M=In and a red shift from closed to open structures. In the latter case the greatest shift is for M=Al (from 6.1 to 4.8 eV from the closed to open rod) and the smallest for M=In

(from 4.3 to 3.8 eV). Thought TDDFT analysis shows the intensities of the light absorption by the closed compounds are much larger than by the open ones. In both cases the lowest spin-singlet state is referred HOMO-LUMO transition.

Elongation Of The Rods

For closed rods the value of energy gap is almost stabilized (6.5 eV) for already 10 rings chain, while for the open rods it is not yet fully stabilized (2.1 eV) even for 38 rings' oligomer that is about 10 nm of length. In contrast with analogues needlerods of 4 group elements[5] or unsaturated BN rods [6] the HOMO and LUMO of the $[HGaNH]_{3n}$ oligomers have no tendencies for delocalization even in case of closed structures. In the Figure 3 band structure of the related polymer is presented by dots. The band gap of the polymer is about 7 eV. HOMO-LUMO gaps of the finite rods are smaller than the band gap of the infinite chain and formed by localized states in its band gap presented by the lines in the Figure 3. While band structure could be extracted from finite oligomer calculations of the 38 rings closed chain, end effects in the open structure of the same length are too significant to consider the chain as periodic.

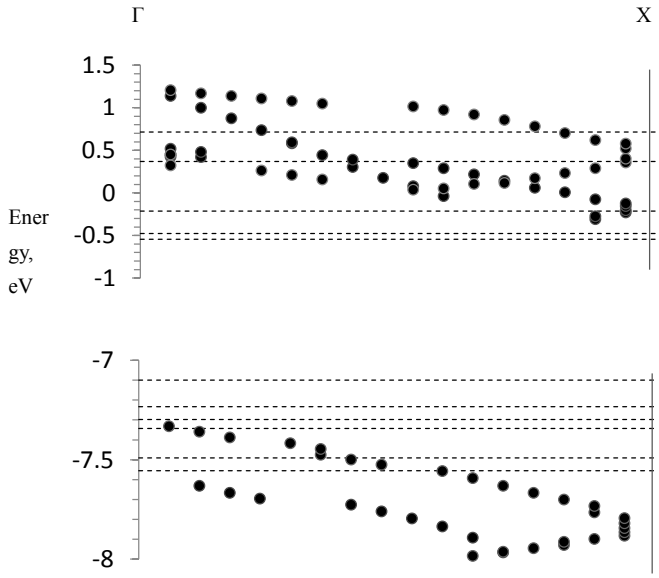


FIGURE 3. Band structure of $[HGaNH]_{3n}$ polymer presented by MOs of closed oligomer with n=38. Circles mark energy dispersion of delocalized MOs in the first Brillouin Zone while energies of localized MOs are depicted by dashed lines.

ACKNOWLEDGMENTS

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Discussion:

K. Morokuma: Which rods are more stable: open or closed one? By how much?

A. V. Pomogaeva: Closed rods are more stable, the energy difference depends on the length of the rod. As far as I remember, both type of rods can exist in the gas phase.

S. Sakaki: In the open rod, molecular orbital is not the same as in crystal structure. For the closed rod it is the same. At what length of the rod the difference disappears?

A. V. Pomogaeva: We still do not know. Even at length around 8 nm the open rod is still very end-affected.

S. Sakaki: This means that HOMO and LUMO are still localized in the open structure.

A. V. Pomogaeva: Yes, they are end-localized.

O-8. Aleksandr Tulub, St. Petersburg State University.

On the stability of magnetic properties of $FeSi_n$ clusters in a framework of MCSCF method.

A.V. Tulub, K.V.Simon

Saint-Petersburg State University

The magnetic properties of iron silicate clusters are of interest in connection with the investigation of the Earth deep interior where magma is in a contact with the iron Earth core. The temperature and pressure is estimated at this depth as about 3500K and 100 GPa and even more. The properties of such matter are now studied experimentally [1,2] .The solids containing Mg, Fe and Si have perovskite like structure $(MgFe)SiO_3$, the forming under the large pressure melt is enriched by heavy elements[1]. The fluid-like matter can be thought as consisting of different size and form clusters, among them the Fe-Si clusters are of a special interest as much as they have magnetic moments. The flow of the fluid can have some macroscopic magnetic effect. We are interested in the clusters containing non zero magnetic moment with minimum number of Fe-atoms.

The electronic structure of FeSi(n) clusters with n=2-8 was studied in [3] by DFT method in (B3LYP/6-311+G*) approach and clusters containing two metal atoms in [4] in the PBE0 approximation. The ground state of small clusters was estimated as the state with the non -zero total spin S.

The theoretical investigation of the stability of magnetic properties includes

I) the calculation the excited electronic states among them the singlet state is of a particular importance,

II) the calculation of ionization potential (I.P.) of a cluster which is to be compared with the energy k_BT for the mentioned temperature,

III) finding the minimum size of a cluster which has in the ground state zero spin value.

The calculation of excitation energy ΔE from the ground state to the first excited singlet state is a relative complicated problem for DFT methods as much as the singlet state is described even for a free Fe-atom as superposition of some number of Slater determinants. The MCSCF method is of importance in obtaining the trusted data.

Clusters Si_n have zero ground state spin and defer in this sense from Si_2 molecule having spin S=1 in it´s $^3\Sigma_g^-$ ground state. The presence of one Fe-atom changes drastically the magnetic moment of a small cluster. The active space for Si was chosen for a correct description of the dissociation limit of Si_2 molecule with the inclusion SOCI excitation from $[4\sigma_g\, 4\sigma_u\, 5\sigma_g\, 2\pi_u]^8$ space to the outer space, basic set is aug cc-pVTZ, the calculation details can be found in our article [5]. We comment the obtained data following the mentioned points.

I) The sequence of different spin states of small clusters reproduce the sequence for a free Fe-atom with the reduced energy intervals. The ground state has the total spin S=2. The excitation energies ($\Delta E/ k_BT$) in k_BT units of are of the order (4-5) for small clusters for S=2→S=0 transition.

II) Ionization Potentials (as the difference of the total energies) are decreasing from the value of I.P. for a free Fe atom (exp.v. 7.9 eV) to the value I.P. =5.4eV for $FeSi_{12}$ cluster, they are large in k_BT units.

III) The minimum size of a cluster with ground spin state S=0 is $FeSi_{12}$ for Fe-atom inside of a cluster, the surface Fe structure has spin S=2.

We conclude that the fluid consisting of $FeSi_n$ clusters is magnetically active at least in the case of a small clusters. The presence of such fluid in a large amount in the Earth deep mantle, possibly connected with a volcanic activity, can create local fluctuations of magnetic properties.

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Discussion:

A. Y. Timoshkin: For clusters with two iron atoms, which geometry is the most favorable: when iron atoms are close to each other or they are apart?

A. V. Tulub: For the small Fe_2Si_3 clusters in the ground state two iron atoms are apart. In the large clusters (18 Si atoms) the outer Si shell is obtained with two bonded iron atoms inside the shell. In this case the molecular state resembles the state of the isolated Fe_2 molecule in terms of the total spin. I would like to say also that there is a number of works which were dedicated to the calculation of the iron clusters of different size. If I put these clusters inside the largest Si cluster I would expect the same ground spin state as for free iron cluster, similar to the situation observed for the small clusters.

A. V. Titov: Did you study how strong the influence of pressure on the properties of the clusters?

A. V. Tulub: The pressure is large, but how to build the model to treat this pressure is a question when I consider the melt as some ensemble of different clusters. I can consider not the free cluster as I has done just now but some compressed state of the cluster. This is only one way that we can do now. Maybe I will find another way when I treat metal properties under high pressure.

O-9. Kazuo Kitaura, Kobe University

Recent development of the fragment molecular orbital method

Kazuo Kitaura

Kobe University

O-10. Alexey Timoshkin St. Petersburg State University.

LEWIS SUPERACIDS AND DONOR-ACCEPTOR CRYPTANDS: FROM NOBLE GAS COMPLEXES TO HYDROGEN SPLITTING

ALEXEY Y. TIMOSHKIN

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Lewis acid-base interactions are cornerstone of any coordination compound. In the present communication results of extensive computational studies on Lewis acid-base interactions of group 13-15 element compounds will be presented. It is shown that pyramidalization significantly increases Lewis acidity of group 13 element derivatives, allowing constructing very strong Lewis acids (Lewis superacids) [1]. Moreover, combination of the pyramidalized donor and acceptor centers in one molecule produces donor-acceptor cryptands (Figure 1), which are predicted to exothermically form complexes with such inert species, as noble gases (including argon) [2]. Bonding in these complexes can be expressed in terms of 3 center 4 electron bonds, similar to that found in noble gas fluorides (Figure 2). Based on these findings, it is expected that donor-acceptor cryptands are capable to form complexes with virtually any element of the periodic table.

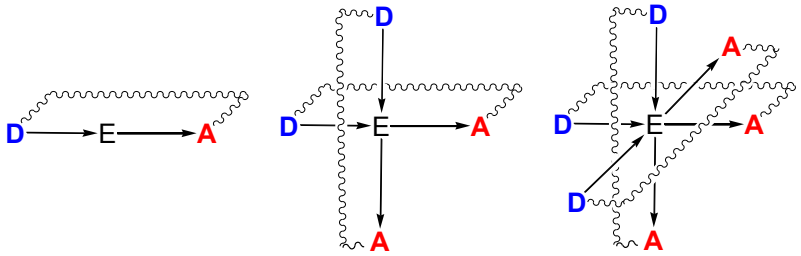

Figure 1 – Schematic representation of the complexes of element E with donor acceptor cryptands. Wavy line represents bridging between donor (D) and acceptor (A) centers.

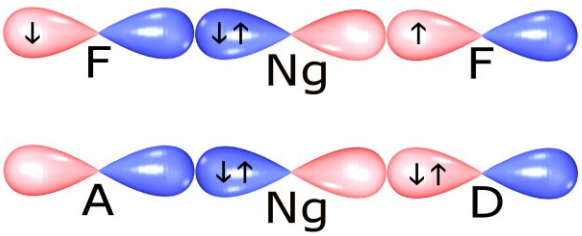

Figure 2 – Schematic representation of the 3-center 4-elecron bond formation in noble gas fluorides and noble gas complexes with donor acceptor cryptand. A – donor, D – acceptor center, Ng – noble gas.

Donor-acceptor cryptands are predicted to exothermically split hydroden molecule [3], which opens perspective for their usage as catalysts for activation of small molecules.

This work was partly supported by Alexander von Humboldt foundation (Germany), Japan Society for the promotion of science and SPbSU grants 12.37.139.2011 and 12.38.255.2014.

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Discussion:

K. Yamashita: You told that the cryptand has not yet been synthesized. How did you design that structure?

A. Y. Timoshkin: I just imagined it. Actually, there is a synthetic approach to make such type of surroundings, developed by Prof. Piers in USA. Not exactly like I proposed, but they made a compound with pyramidalized boron atoms in strained environment. .

K. Yamashita: Proposed framework has a very strong strain.

A. Y. Timoshkin: Yes, the structure is highly strained. It is not realistic from the chemical point of view, as the bridges contain just triple bonds. It is not practical, it is just to get connection between donor and acceptor parts. At first, I thought that strain is important and structure should be rigid. But now I think the strain is not important because this cage should be able to adjust according to the interaction. It adjusts quite a lot, the reorganization energy is quite large. So I think now that bridge should not be rigid and maybe just CH_2 units would be more practical.

O-11. Jun-ya Hasegawa, Hokkaido University

Excitation Energy Transfer Pathways in Bridged Donor-Acceptor Systems

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Introduction

Excitation energy transfer (EET) is a fundamental process in photochemistry and photobiology. EET is also a key process in industrial products such as light emitting diodes (LED) and solar cells. In fluorescence (or Förster) resonance energy transfer (FRET), EET quenches an emission of an excited molecule and provides fluorescence at another emitting molecule. In this study, a computational method for calculating electronic coupling and pathway of electron transfer (ET) has been extended to that for EET[1]. The method was applied to model peptides and conjugated molecules to analyze their electronic couplings as well as the direct and through-peptide terms[1,2]. We have also extended the method to investigate the pathway of triplet EET and compared with that of the singlet EET[3].

Computational method

To calculate electronic coupling between donor and acceptor, we generalized a molecular orbital (MO)-based method for electron transfer to that based on Slater determinants.

$$T_{IF} = \sum_{ai,bj} C_{ai}^{I} \langle ai | E - \hat{H} | bj \rangle C_{bj}^{F} \tag{1}$$

C_{ai}^{I} and C_{bj}^{F} are CI coefficients for the initial- and final-state wave function, and E is a tunneling energy. The method is, therefore, applicable to EET, which involves the transfer of an electron-hole pair. To represent EET donor, acceptor, and bridge states, we adopted recently developed localized molecular orbitals (LMOs) for constructing locally excited determinants[4]. The LMO approach provides a chemically meaningful interpretation of how each local excitation on the bridge contributes to the total electronic coupling of the EET. To analyze EET pathway, we defined a course grained tunneling flux between fragments *M* and *N*.

$$K_{M,N} = \sum_{ai \in M} \sum_{bj \in N} \hbar \tag{2}$$

$$J_{ai,bj} = \frac{1}{\hbar} \left(C_{ai}^{I} C_{bj}^{F} - C_{ai}^{F} C_{bj}^{I} \right) \langle ai | \hat{H} | bj \rangle \tag{3}$$

Result and discussions

We applied the method to six model peptides and calculated their electronic couplings as well as the direct and through-peptide terms. Although the through-peptide term is usually negligibly small compared with the direct term, it can dominate the EET reaction in appropriate situations. The direct term dominates in

long-range interactions because the indirect term decays in shorter distances.

Next we investigated situations where the indirect EET (the so-called superexchange mechanism) can be crucial. Donor(D)−linker−acceptor(A) molecular systems that include various linker types, linker lengths, and tunneling energies were calculated. In a model compound, the superexchange term can be up to 4 times larger than the direct term when the energy of the excited state at a linker unit is close to the tunneling energy and when the interactions between these excited states are strong. The ratio of the indirect term to the direct term is greatest at a certain D−A distance because the number of multistep terms increases and the sizes of multistep indirect terms decay exponentially. Single-step indirect terms, which exhibit a polynomial decay, dominate the indirect term for larger D−A distances. The result of the pathway analysis showed that the exciton states mediate EET, and therefore, the coupling between the local excited states is driven by the excitonic interaction, even in the superexchange terms.

The donor−acceptor electronic coupling for a bridge-mediated triplet EET was analyzed to determine the tunneling pathway using eq. (2). In the singlet EET, the electronic coupling is primarily composed of direct coupling between the donor and acceptor. In contrast, the triplet EET is dominated by superexchange interactions because the Förster-type interaction becomes forbidden. The triplet EET tunneling pathways are characterized as a sequentially coupled hole and electron transfer (CHET) for both direct and bridge mediated EETs.

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Discussion:

K. Morokuma: In some views the excitation transfer depends very sensitively on geometry of individual molecules or intermolecular geometry. In your analysis, where is geometry coming in?

J-Y. Hasegava: We keep the same geometry. But to understand geometry difference we took different donor-acceptor pairs. We do not move the fragments, but we take different orientations. One interesting point is that for the model 3-4 there is short distance between fragments but the orientation of the donor and acceptor fragments is somehow unfavorable and as a result, electron coupling decreases.

O-12. Masataka Nagaoka, Nagoya University

Japan-Russia Joint Symposium "Chemical Theory for Complex Systems"
Sept. 19, 2014, St. Petersburg, Russia

Toward Controlling Complex Chemical Reactions in the "Molecular Aggregation States" -From Multiscale Simulation to Computational Molecular Technology-

Masataka Nagaoka [a),b),c)]

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We demonstrate a new efficient hybrid MC/MD reaction method with a rare event-driving mechanism as a practical 'atomistic' molecular simulation of large-scale chemically reactive systems (Figure 1). Application of the method to (R)-2-chlorobutane molecules in N,N-dimethylformamide (DMF) molecules starting in the optical pure state (100% e.e.) was found to successfully provide such an atomistic state with ~0% e.e., the expected purity of (R)- to (S)-enantiomers of the racemic mixture in chemical equilibrium [1].

This hybrid MC/MD reaction method is promising for various application studies in complex chemically reacting systems, e.g., the formation process of solid electrolyte interphase (SEI) film in lithium-ion batteries (LIB) [2]. It was understood that the SEI film formation is strongly sensitive to the small structural difference of electrolyte molecules at the microscopic level.

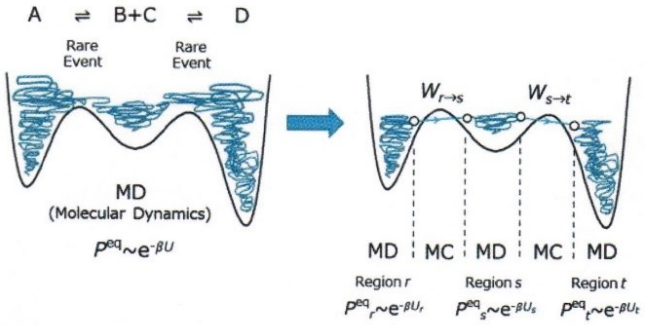

Figure 1. Schematic representation of the hybrid MC/MD reaction method. The curly curves represent the molecular dynamical (MD) moves in phase space following the equations of motion, while the straight lines with arrows represent the Monte Carlo (MC) moves (or transitions) of the system (right figure), whose dynamical moves would be extremely rare events. In the left figure, the configurational distribution in equilibrium p^{eq} is proportional to the exponential factor $\exp[-\beta U]$ where U is the global potential function. The right figure shows regional distributions, e.g., $p_r^{eq} \approx \exp[-\beta U_r]$ in region r, etc. The connecting points of the two kinds of moves (open circles) are selected according to the criteria for chemical reaction occurrence. Note that they do not represent real connections since these points correspond to almost identical states in configuration space but not in momentum space and with different configurational gradients. $W_{r\to s}$ and $W_{s\to t}$ are the transition probabilities from state r to s and from s to t, respectively [1].

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O-13. Alexander Khlebnikov, St. Petersburg State University.

How DFT calculations can help synthetic organic chemist

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Currently DFT calculations, in relatively simple versions, provided a sufficiently accurate data on the molecular geometry and energy parameters of the reactions. Considering that now such calculations can be implemented with acceptable time consuming even for complex systems, organic chemists increasingly use a mixed type of experiment: "PC→flask / flask→PC ".
Various topics of the use of the calculations that make life easier and more effective for synthetic chemist will be discussed, based on the recent experience of our group (http://www.chem.spbu.ru/org/1058-strain_group.html).

Study of the feasibility of the stereoselective synthesis of complex molecules. (A. S. Konev, A. F. Khlebnikov, H. Frauendorf. Bisaziridine tetracarboxylates as building blocks in the stereoselective synthesis of C60-fullerene diads and dumbbell-like bis-C60-fullerene triads. *J. Org. Chem*., 2011, 76, 6218-6229, DOI: 10.1021/jo2009627; A. S. Konev, A. F. Khlebnikov, T. G. Nikiforova, A. A. Virtsev, H. Frauendorf. Synthesis and spectroscopic and electrochemical properties of an axially symmetric fullerene-porphyrin dyad with a rigid pyrrolo[3,4-c]pyrrole spacer. *J. Org. Chem*., 2013, 78, 2542-2552, DOI: 10.1021/jo302763a; A. S. Konev, A. F. Khlebnikov, P. I. Prolubnikov, A. S. Mereshchenko, A. V. Povolotskiy, O. V. Levin, A. Hirsch. Synthesis of New Porphyrin–Fullerene Dyads Capable of Forming Charge-Separated States on a Microsecond Lifetime Scale. *Chem. Eur. J.* 2014, 20,. DOI: 10.1002/ chem.201404435).

Selection of a suitable reaction partners, which allow synthesizing the target compounds, when that is difficult to do using conventional concepts of Organic chemistry. (I. J. Kobylianskii, M. S. Novikov, A. F. Khlebnikov. Formation and reactivity of gem-difluoro-substituted pyridinium ylides: Experimental and DFT investigation. *J. Fluor. Chem*. 2011, 132, 175-180, DOI: 10.1016/j.jfluchem.2010.12.013).

Finding new reaction pathways. (A. F. Khlebnikov, M. S. Novikov, Y. G. Gorbunova, E. E. Galenko, K. I. Mikhailov, V. V. Pakalnis, M. S. Avdontceva. Isoxazolium N-ylides and 1-oxa-5-azahexa-1,3,5-trienes on the way from isoxazoles to 2H-1,3-oxazines. *Belst. J. Org. Chem.* 2014, 10, 1896–1905, doi:10.3762/bjoc.10.197).

Determining structure of tautomers and position of tautomeric equilibrium. (Khlebnikov, A. F.; Tomashenko, O. A.; Funt, L. D.; Novikov, M. S. Simple Approach to Pyrrolylimidazole Derivatives by Azirine Ring Expansion with Imidazolium Ylides. *Org. Biomol. Chem*. 2014, 12, 6598-6609, doi: 10.1039/c4ob00865k).

Recommendation how to store some unstable compounds. (Khlebnikov, A. F.; Novikov, M. S.; Pakalnis, V. V.; Iakovenko, R. O.; Yufit D. S. Domino reactions of 2*H*-azirines with acylketenes from furan-2,3-diones: Competition between the formation of *ortho*-fused and bridged heterocyclic systems. *Belst. J. Org. Chem*. 2014, 10, 784-793, doi:10.3762/bjoc.10.74).

Discussion:

Jun-ya Hasegawa: As I understand, if you want original compound, you decompose azirine. Am I correct? I understand that you store this compound as azirine and then you decompose it.

A. F. Khlebnikov: Probably not, because the problem is to store azirine. It is three-membered ring, so it is very strained, so it is unstable. It is strange but it decomposes in fridge, and in deep fridge, and so on. A lot of publications claim that it is difficult to store. We also faced this problem experimentally, and now from our computations we know how to store this compound.

Jun-ya Hasegawa: When you calculate and look at the reaction pathway, how much the activation energy is stable? How your computations correspond to experimental decisions?

A. F. Khlebnikov: We perform very simple calculations: we calculate free energies of starting compound, transition state and final product. From our experience, the barrier above 30 kcal mol^{-1} is too large for the reaction to proceed effectively. Less is OK. So, if in computations we for example obtain reaction barrier of 40 kcal mol^{-1} we usually never do an experimental work. Of course, probably we will make a mistake because we think the mechanism is like we computed, but probably reaction can proceed by other mechanism.

We also used calculations to find out how to change substituents in our porphyrine –fullerene ensemble to enlarge the lifetime of charge separated states. Of course, these computations are not so complex as you do, but we can find some recommendations with this simple calculations how to change substituents. We succeeded now to 3 ps, and probably we will find system which have much longer lifetime.

K. Morokuma: I am very proud that I did some theory for theoretical calculations that are helping you. We also sometimes have the problem, and we think on it and find new pathway, like you showed. That is exactly that we do nowadays and it is very nice to hear.

A. V. Pomogaeva: Do you think that B3LYP/6-31G* level is sufficient?

A. F. Khlebnikov: According to our experience, it is better to compute the real molecule at lower level than some part of molecule at higher level. Practically, this level of theory is enough for organic chemist. Of course, sometimes we study rearrangements, and sometimes we make single point computations at higher level. For the geometry optimization, this level is sufficient.

Poster presentations:

P-1. **Yuri Demidov**, St. Petersburg Nuclear Physics Institute

CHEMICAL PROPERTIES OF SUPERHEAVY ELEMENT 113: FIRST PRINCIPLES BASED MODELING

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After successful "chemical" identification of copernicium (element 112) and flerovium (element 114) by the thermochromatography on gold technique, investigation of element 113 (E113) properties is of top interest. First experimental results on E113 chemistry were recently obtained in FLNR JINR (Dubna) [1]. In this experiment five decay chains of ^{284}E113 were registered and the value of adsorption enthalpy of E113 single atoms on gold surface was estimated: $-\Delta H_{Au}$ (E113) > 60 kJ/mol. Model experiments with lighter homologues of E113: thallium and indium were also performed [2]. In the presence of water the formation of Tl and In compounds (probably TlOH and InOH) was observed. In this work we stady the adsorption of E113 single atoms on stable gold surface, molecular structures and properties of E113OH and TlOH and the possible mechanism of their formation.

Adsorption of single E113 atom on gold surface was investigated in our recent work within a cluster model [3]. Several gold clusters (Au_n) comprising up to 58 atoms were chosen to simulate the adsorption site of E113 on the stable (111) gold surface. According to a series of preliminary calculations, the position of E113 atom over the atom of Au in the second layer of the cluster is energetically preferable. Since the stabilization of binding energies upon the increase of cluster size can be occasional, the convergence was additionally monitored through both analyzing Bader net charges of the E113 and neighboring Au atoms and equilibrium distance E113/gold surface as functions of the cluster size. The resulting adsorption energy estimates lie within the range 106±10 kJ/mol. According to experimental data [2] the adsorption energy of single Tl atoms on gold surface is much larger, 270±10 kJ/mol.

Calculations were performed within the two-component shape-consistent small-core pseudopotential model [4] and employed the non-collinear version of relativistic density functional theory (RDFT) to treat electronic correlations [5].

To evaluate the probability of E113OH molecules formation in the experiment described above, we performed a comparative study of E113OH and TlOH properties. We employed the combined approach involving scalar relativistic coupled cluster (CCSD(T)) calculations with the extapolation to the complete-basis-set limit and the evaluation of spin-dependent effects and zero-point energies at the RDFT level. The energetics of the simplest reactions

$$M + H_2O \rightarrow MOH + H \ (M = E113, Tl).$$

was estimated. Both reactions are energetically unfavorable: ΔH_0 =128 kJ/mol for M = Tl and 267 kJ/mol for M = E113. The equilibrium distance E113–O in E113OH is 2.28 Å, the corresponding value for Tl is 2.15 Å. The complexes of E113 and Tl atoms with H_2O singe molecules (M–H_2O) are also weakly bounded and unstable. The formation of E113OH and TlOH via the reactions of E113 and Tl atoms with small water clusters seems more probable. For this reason the interaction of E113 and Tl single atoms with small water clusters (up to 5 molecules) was investigated by RDFT methods; some resulta are given in Figure 1. Recently the mechanism of NaOH molecule formation involving such reactions was established [6]. Formation energies of E113OH and TlOH molecules in these reactions decreases significantly: 85 ± 10 kJ/mol for TlOH and 78 ± 10 kJ/mol for E113OH. We observed a weak dependence of E113OH formation energy on water cluster size. Therefore, E113OH formation by reactions of E113 with water vapor seems not probable.

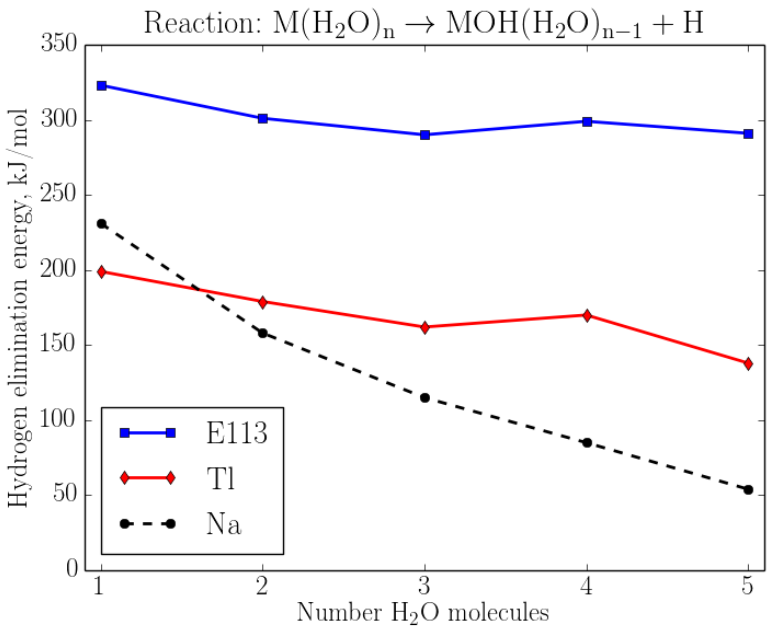

Figure 1: Energetics of hydroxide molecules formation by reactions with small water clusters.

Thanks are due to Dr. Kenro Hashimoto, Dr. Robert Eichler and Dr. Alex A. Rusakov.

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P-2. **Christina Reshetova**, St. Petersburg State University.

Spectroscopic and quantum-chemical investigation of the Ru(II) chloro- and nitro-bis-(bipyridyl) complexes with 4-substituted pyridine ligands

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Ruthenium(II) complexes with polypyridine ligands have a unique combination of photophysical, photochemical and redox properties, and chemical stability. The interest in these compounds is mainly due to their prospective use as “antenna complexes” in solar energy conversion, biotechnology, design of luminescent sensors and photochemical molecular devices. Directed synthesis of new complexes with a set of predetermined characteristics requires understanding the interrelation between the composition of the coordination sphere and the electronic structure of the compounds and their photophysical parameters measured in experiment. The study of series of complexes in which the composition of the inner coordination sphere is purposefully varied is an efficient method of obtaining the information.

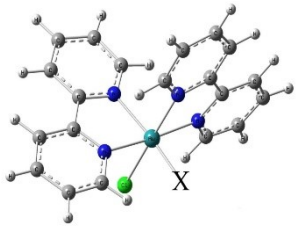

Fig. 1. *The structure of ruthenium(II)*

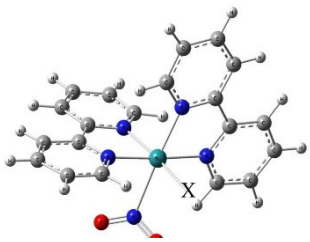

Fig. 2. *The structure of ruthenium(II)*

In the preceding investigation [1] absorption and luminescence spectra of ruthenium(II) chloro- and nitro-complexes (fig. 1, 2) cis-$[Ru(bpy)_2(X)Cl]^+$, cis-$[Ru(bpy)_2(X)NO_2]^+$ [bpy=2,2'-bipyridyl; X — pyrazine, pyridine, 4-aminopyridine, 4-picoline, isonicotinamide, 4-cyanopyridine, 4,4'-bipyridyl, or trans-1,2-bis(4-pyridyl)ethylene, mapy] in alcoholic (EtOH–MeOH 4:1) solutions are studied at 77 K. The linear correlation between the energy of the lowest state ^{3}MLCT $d_\pi(Ru)\rightarrow\pi^*(bpy)$ of the complexes and the parameter pK_a (protonation constant expressed in terms of the Hammet constants is used as an experimental characteristic of the donating–accepting ability of a free pyridine ligand, whose nitrogen atom reveals basic properties in this paper) of the free 4-substituted pyridines is established.

In current work, several quantum-chemical calculations of Ru(II) complexes were performed using program Gaussian 09. Calculations were performed within the bounds of DFT, using 6-31G(d) and LanL2DZ basis and B3LYP functional. Operations performed frequency analysis, geometry optimization, single-point energy calculation, an excited state calculation using the time-dependent DFT method, charge distribution for complexes and free ligands and phosphorescent emission of complexes from the lowest triplet state to the ground state.

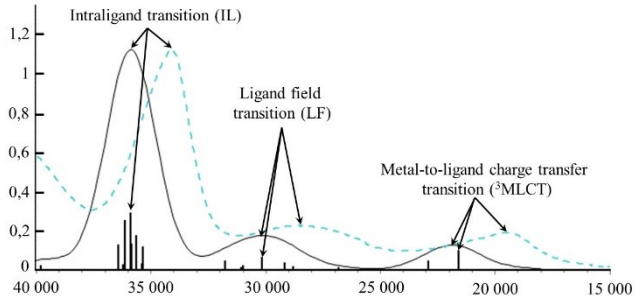

Fig. 3. *Absorption spectra of* ***cis-[Ru(bpy)$_2$ApyCl]$^+$*** *in 4:1 EtOH–MeOH (- - -) and calculation spectra in ethanol solution (vertical lines and ——).*

Absorption spectra

A comparison of the experimental and calculated absorption spectra (fig. 3) shows that calculated complexes' values of shift of the absorption bands are equal in order of magnitude to the experimental data.

Each line of the absorption spectra of the Ru(II) complexes were identified to one of three types of transition IL, LF or ^{3}MLCT.

Investigation of ^{3}MLCT state:

In current work, the energy's values of phosphorescent emission from ^{3}MLCT states were calculated as an energy difference between the lowest triplet state and the ground state of optimized complexes for both range of Ru(II) complexes. A comparison of the experimental and calculated energy's values of phosphorescent emission of complexes shows a good correlation (fig. 4, 5).

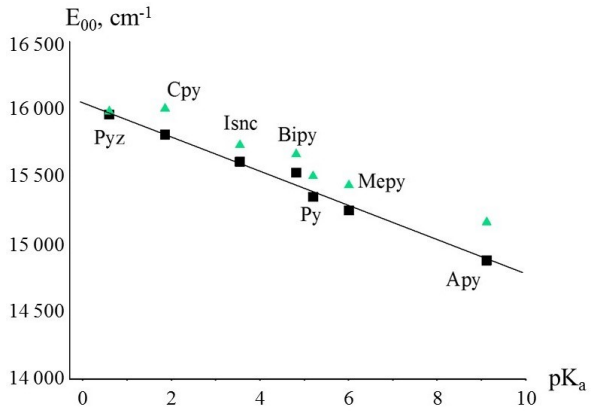

Fig. 4. *The correlation between the energy of the lowest state ^{3}MLCT d_π(Ru)→π^*(bpy) of the chloro-complexes (■), the calculation energy of the lowest state ^{3}MLCT (▲) in ethanol and the parameter pK$_a$ of the free 4-substituted pyridines.*

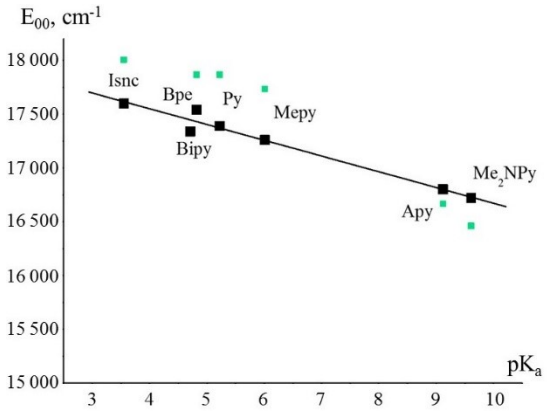

Fig. 5. *The correlation between the energy of the lowest state ^{3}MLCT d_π(Ru)→π^*(bpy) of the nitro-complexes (■), the calculation energy of the lowest state ^{3}MLCT (■) in ethanol and the parameter pK$_a$ of the free 4-substituted pyridines.*

Analysis of this data shows the difference between experimental and calculation values of phosphorescent emission 157 cm^{-1} for chloro-complexes and 294 cm^{-1} for nitro complexes.

Charge distribution:

Charge distribution of nitrogen atom of 4-substituted pyridine ligands coordinated to the Ru(II) were obtained by the NPA option of the Gaussian 09.

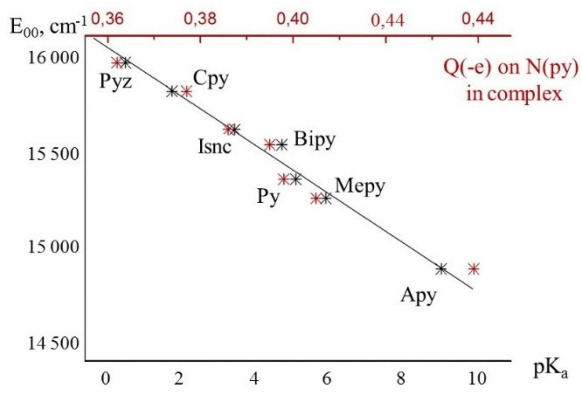

Fig. 6. *Dependence of the electronically excited ^{3}MLCT states of chloro-complexes on the values of pK_a of the ligands (✳) and correlation between the energy of this states and charge distribution of nitrogen atom of 4-substituted pyridine ligands coordinated to the Ru(II) (✳).*

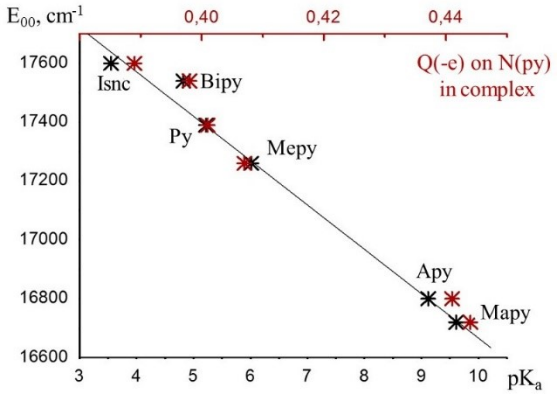

Fig. 7. *Dependence of the electronically excited ^{3}MLCT states of nitro-complexes on the values of pK_a of the ligands (✳) and correlation between the energy of this states and charge distribution of nitrogen atom of 4-substituted pyridine ligands coordinated to the Ru(II) (✳).*

According to obtained results one can conclude, that experimentally observed shift of the value of phosphorescent emission (E_{00}) for Ru(II) complexes significantly due to the variation of charge distribution of nitrogen atom of 4-substituted pyridine ligands coordinated to the Ru(II) and related with this variation the energy shift of d-orbital of ruthenium(II) (fig. 6, 7).

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P-3. **Anna Lisovenko**, St. Petersburg State University.

Influence of Donor-Acceptor Interaction on Hydrogenation of Borazine and Polyborazines

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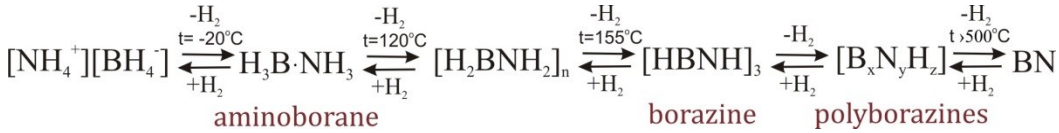
In the last years, boron-nitrogen systems, in particular, aminoborane $H_3B{\cdot}NH_3$ (AB), attract growing interest as solid carriers for chemical storage of hydrogen [1]. AB decomposes on heating with the liberation of hydrogen and formation of amido- and imidoboranes and boron nitride (at elevated temperature). Borazine $[HBNH]_3$ and polyborazines $[B_xN_yH_z]$ are important intermediate products of AB dehydrogenation:



Hydrogenation processes of borazine and polyborazines are of significant interest for regeneration of hydrogen fuel. The hydrogenation reactions of imidoboranes are extremely endothermic and possess high activation energy, which is attribute to aromatic stabilization of 6-membered B_3N_3 cycles. To facilitate hydrogenation of borazine and polyborazines, we propose to disrupt their conjugated π-system by complexation with Lewis acids (LA) and bases (LB) [2]. Complexes of alkyl-substituted borazines with such LA as AlBr3 and GaCl3 have been made in the laboratory and structurally characterized [3]. In the present work, data of quantum chemical calculations are used to consider an influence of complexation of borazine and polyborazines with Lewis acids on the hydrogenation processes of their heterocycles.

Table 1. Thermodynamic characteristics of the hydrogenation process of borazine, its complex with $AlCl_3$, its complex with $AlCl_3$ and NH_3 [4]. B3LYP/TZVP level of theory.

Step	Reaction	without D; without A		without D; A = $AlCl_3$		D = NH_3; A = $AlCl_3$	
		$\Delta_rH^o_{298}$, kJ mol^{-1}	$\Delta_rG^o_{298}$, kJ mol^{-1}	$\Delta_rH^o_{298}$, kJ mol^{-1}	$\Delta_rG^o_{298}$, kJ mol^{-1}	$\Delta_rH^o_{298}$, kJ mol^{-1}	$\Delta_rG^o_{298}$, kJ mol^{-1}
1	$D{\cdot}B_3N_3H_6{\cdot}A + H_2 = D{\cdot}B_3N_3H_8{\cdot}A$	127.6	160.1	57.6	95.3	33.1	74.8
2	$D{\cdot}B_3N_3H_8{\cdot}A + H_2 = D{\cdot}B_3N_3H_{10}{\cdot}A$	18.6	54.0	5.2	46.9	-12.8	28.3
3	$B_3N_3H_{10} + H_2 = B_3N_3H_{12}$	-31.5	7.0	-	-	-	-

The hydrogenation procersses of borazine, polyborazines, and their donor-acceptor complexes with a model Lewis acid AlCl3 were studied by the B3LYP/TZVP quantum chemical method. For the first time, the complexation was found to considerably decrease endothermicity, as well as activation energy of hydrogenation processes of borazine and polyborazines (table 1). This allows us to recommend the use of Lewis acids as catalysts in the processes of regeneration of spent hydrogen fuel. Addition of a hydrogen molecule during hydrogenation of polyborazines and boron-nitrogen analog of graphene will preferably occur at the peripheral atoms of the heterocycles. The reactivity of the heterocycle with respect to hydrogenation is expected to decrease with the decrease in the amount of peripheral atoms as the size of the heterocycle increases.

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P-4. **Dmitri Doinikov**, St. Petersburg State University.

Requirement of Grimme's dispersion correction for DFT calculations of B–N complexes

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In modern inorganic chemistry a novel class of complex compounds exists, called frustrated Lewis pairs[1] (FLPs). FLPs are sterically crowded Lewis complexes, allowing them to use space between donor and acceptor centers to catch and activate or cleave bonds in small molecules (dihydrogen, alkenes, green gases etc.). To properly apply computational chemistry methods to FLPs one should take steric interactions into account. To perform this we have used Grimme's dispersion correction[2] and shown its impact on complexation energies of a number of Lewis pairs.

We calculated complexation energies (D+A = DA) for a typical FLP system $B(C_6F_5)_3$ – Lut and its non-crowded analogue complex $B(C_6F_5)_3$ – Py (Fig.1) and estimated contribution of steric interactions into complexation energy to be 57 kJ. It was found out that the closest to the experimental B–N bond lengths (1.661(2)[3] and 1.628(2)[4] Å for Lut and Py systems resp.) are obtained with B3LYP-D3/def2-SVP level of theory (1.6897 and 1.6441 Å resp.).

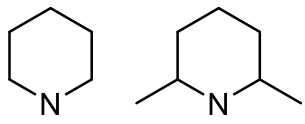

Fig. 1. Pyridine (Py) and 2,6-Lutidine (Lut)

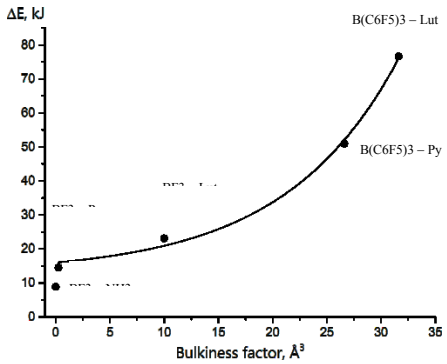

Fig. 2. Complexation energies for a number of B–N systems with different sterical factor.

We calculated Grimme's dispersion corrected complexation energies for $B(C_6F_5)_3$ – Lut and $B(C_6F_5)_3$ – Py systems and a number of analogues complexes with a different degree of steric crowdness. We have introduced steric factor, representing degree of a steric crowdness between donor and acceptor centers in $Å^3$ and based on Van Der Waals radii. We found out that the difference between corrected and uncorrected complexation energy had very slightly depended

on basis set (def2-SVP, def2-TZVPP) and mostly depended on steric factor (Fig. 2).

We calculated complexation energies for $B(C_6F_5)_3$ – Lut and $B(C_6F_5)_3$ – Py systems for different levels of theory (Fig. 3,4). Results for corrected B3LYP-D3 method lie nearer to M06 methods (that include dispersion correction themselves), than to uncorrected B3LYP. We may conclude, Grimme's dispersion correction is essential for FLP-related calculations.

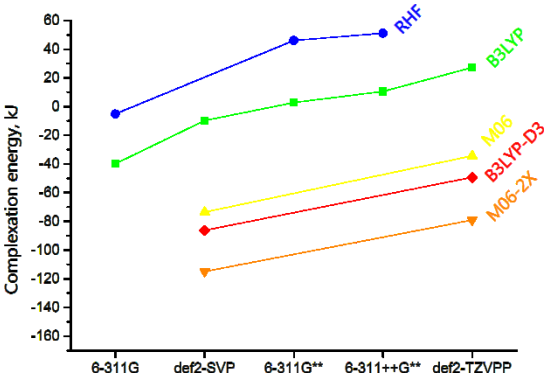

Fig. 3. Complexation energies calculated on different theorylevels for B(C6F5)3 – Lut system.

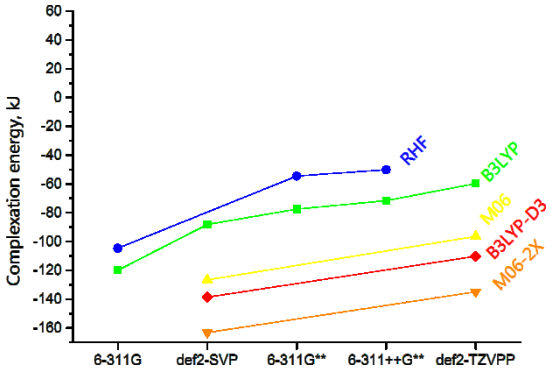

Fig. 4. Complexation energies calculated on different theorylevels for B(C6F5)3 – Py system.

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(2) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. *J. Chem. Phys.* **2010**, *132*, 154104.
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(4) Focante, F.; Mercandelli, P.; Sironi, A.; Resconi, L. *Coord. Chem. Rev.* **2006**, *250*, 170–188.

P-5. **Ilya Kopanichuk,** St.-Petersburg State University

Adsorption of Lennard-Jones fluid in finite slit-shaped pores

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Study of a gas adsorption into the pore by a computer simulation method gives us a detailed information about an adsorption mechanism. A lot of calculations were made with simplified models of infinitely long pores, however, real ones are finite. The aim of this work is an investigation of boundary effects in nanopores. As boundary effects we mean the difference in isotherms and mechanisms of adsorption between finite and infinite pores. So we study adsorption of the fluid in pores with a different section to compare mechanisms of a filling infinite, asymmetric and symmetric pores (see Fig. 1.) with the fluid.

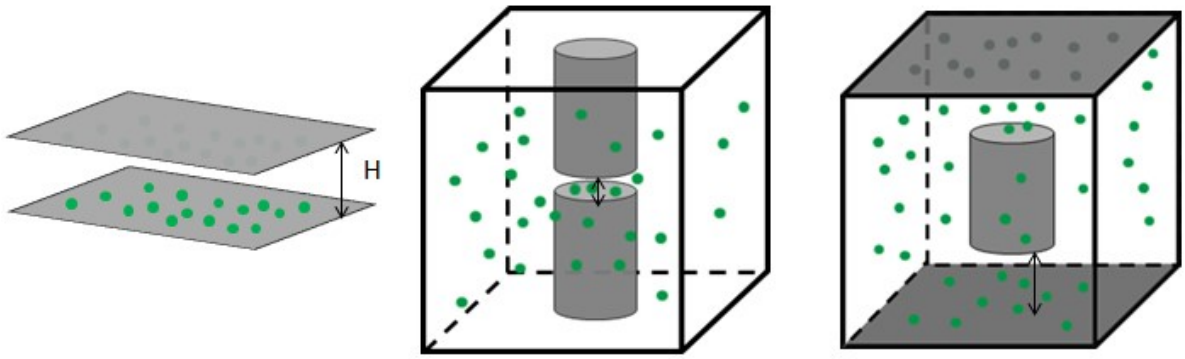

Fig. 1. Infinite, symmetric and asymmetric pores. Grey surfaces and cylinders are adsorbents, spheres are molecules of an adsorbate.

Calculations were made by GCMC method, T = 111K. The chemical potential has been recalculated to the pressure later with the ideal gas equation of state. As an adsorbate were used LJ fluid with parameters of methane: $\sigma = 0.373$ nm, $\varepsilon/k_B = 148.1$ K. The adsorption field of the infinite pore were described by the 10-4-3 potential. Finite slit-shaped pores were made from the graphite cylinder like the MWCNT with flat ends. The radius is equal to 6 σ, the width H is varied from 6 to 12 σ.

Finite slit-shaped pores demonstrate strong boundary effects on the local fluid density especially for the low pressure: amount of the fluid absorbed in the symmetrical pore is lower than amount absorbed in asymmetrical and infinite pores. There is no observed boundary effects at high pressure. Boundary effects get lower with the rising of the pore width. The difference between the fluid density in H = 9 σ and H = 12 σ is less than between H = 6 σ and H = 9 σ, so it decreases with the rising of the pore width. Hysteresis at H = 6 is more emphasized for symmetric and infinite pores than for the asymmetric one.

P-6. **Anastasia Sizova**, St. Petersburg State University

Computer simulation of CO_2/CH_4 mixture adsorption in porous materials: effects of pre-adsorbed water

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Grand Canonical Monte Carlo (GCMC) simulations were used to compare the mechanisms of adsorption of CH_4/CO_2 mixture in slit and cylindrical silica and carbon pores in the presence of preadsorbed water. The widths of the slit pores were equal to 8, 20 and 40 Å. Cylindrical pores were represented by **SBA-15** siliceous material with mesopores of 39 Å diameter and microchannel connection (diameter 8 Å) and **CMK-5** amorphous carbonaceous adsorbent with cylindrical mesopores (diameter 32 Å) and carbon microrods.

Simulations were carried out at 298 K (cylindrical pores) and 318 K (slit pores) for pressures up to 50 atm. CH_4/CO_2 mixture containing 50% of carbon dioxide was considered. To study the effect of moisture, certain amounts of water were placed into the simulation cell. During gas adsorption simulations the number of water molecules was fixed, but they were allowed to move and rotate. All atoms of the adsorbent were frozen during the simulation.

All adsorbents under investigation are selective to carbon dioxide: partial capacities of methane are much lower than those for CO_2. While the behavior of the dry adsorbents is quite similar, it differs drastically in the presence of preadsorbed water.

For all silicas in the presence of preadsorbed water the adsorption capacity for carbon dioxide decreases significantly, while the capacity for methane remains almost constant. The wider the pore, the more the difference in gas adsorption capacity. Selectivity to CO_2 also diminishes in wet siliceous adsorbents.

Pore size and shape govern the behavior of the carbons in the presence of pre-adsorbed water. Capacity of 8 Å wet pore is lower than that of the dry pore in the whole range of pressures,

which is due to the accessible volume reduction by preadsorbed water molecules in the pore. Capacity of wet 20 Å pore is not lower than that of dry one up to ca. 30 atm. In 40 Å pore volume limitation does not arise, and capacities for wet and dry adsorbents are equal for all pressures considered in this work. In cylindrical carbon mesopores an increase of gas capacity in the presence of water is observed (**Fig.1**). This increase is due to the higher partial CO_2 adsorption capacity in wet pores. Methane capacity is almost unaffected by the presence of water. Selectivity coefficients to CO_2 for all wet carbons are higher than for the dry ones.

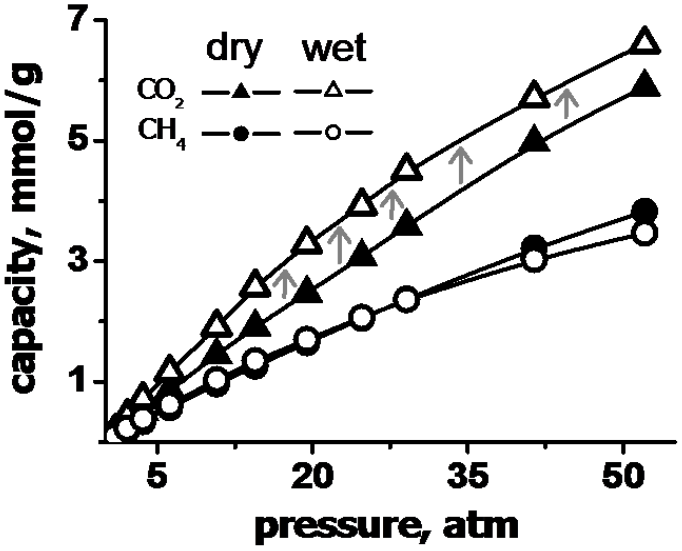

Fig. 1. Partial CO_2 and CH_4 adsorption isotherms for dry and wet CMK-5

The effects observed can be explained in terms of interaction energies between carbon dioxide and dry or wet adsorbent. Interactions with siliceous adsorbents are very strong, the presence of water weakens them because water molecules cover the surface of the adsorbent. Water in carbonaceous adsorbents forms clusters, and a large part of the surface remains free for gas adsorption. Interactions with water are favorable for carbon dioxide, thus adsorption in wet carbons is more efficient than in dry carbons.

P-7. **Maria Novozhilova**, St. Petersburg State University.

Spectroelectrochemical Studies of Electrodes Modified by Polymer Complexes of Nickel with Schiff Bases.

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Polymer complexes of transition metals with SalEn-type ligands possess a number of unique properties, such as high redox conductivity, electrochromic behavior, and selective catalytic activity in heterogeneous reactions including electrocatalysis, which make them suitable for application in a variety of systems. They are used for electrocatalytic, optoelectronic and sensor devices. In the literature, it is proved the effectiveness of polymeric nickel complexes with Schiff bases for modifying electrodes double-layer supercapacitors. The main idea of this work is obtaining new data on the mechanism of conductivity of polymer complexes of nickel with tetradentate Schiff bases of a salen type.

In the literature there is no common model that describes the mechanism of charge transport in these polymers. To solve this problem we use a combined experimental and computational approach, which connected together structure, electrochemical and optical properties of polymers. The experimental results and quantum chemical calculations demonstrated the crucial role of exogeneous ligands in the redox transformations of polymers.

Redox transformation of various polymeric [Ni(SalEn)] type complexes were studied by cyclic voltammetry, UV-visible spectroscopy, in-situ differential voltabsorptometry and compared with DFT calculation predictions. It was demonstrated that in acetonitrile-based supporting electrolyte solutions oxidation of such complexes, regardless of ligand substituents, proceeds by two routes, leading to formation of the two oxidized forms ***Ox1*** and ***Ox2***.

Complicated electrochemical response of studied substituted polymers can be explained in scope of this model without any additional assumptions, taking into account interconversion of the forms ***Ox1*** and ***Ox2***. Formation of the first form can be easily assigned to polaron in terms of conducting polymers charge transfer model. However, formation of the second oxidized form can not be explained by this model, but correlates with observations of Ni(III) species made on monomeric complexes with axial ligands. Acetonitrile and phenyl moieties of neighboring polymer layers may act as such ligands, and as Ni(III) was never detected in dry films by magnetic resonance methods, the solvent must play an important role in such coordination.

P-8. **Pavel Snegurov**, St. Petersburg State University.

Molecular dynamics simulation of ionic conductivity in yttria-stabilized zirconia.

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Molecular dynamics (MD) simulations were carried out to study ionic transport in cubic and tetragonal $[ZrO_2]_{1-x}[Y_2O_3]_x$ solid oxide (yttria-stabilized zirconia, YSZ) at 1200 K, 1500 K, and 2000 K for samples containing up to 10 mol.% of Y_2O_3. Calculated oxygen diffusion coefficients were averaged over twenty random cation distributions for each YSZ composition to ensure correct evaluation of the dependence of diffusivity on yttria content. The data obtained from MD simulations were used in conjunction with experimental phase diagram (Figure 1) to estimate the oxygen transport performance of YSZ samples, including those containing more than one phase. For heterogeneous samples (T+C and T+M) the quantities of coexisting phases were obtained from the phase diagram using the lever rule.

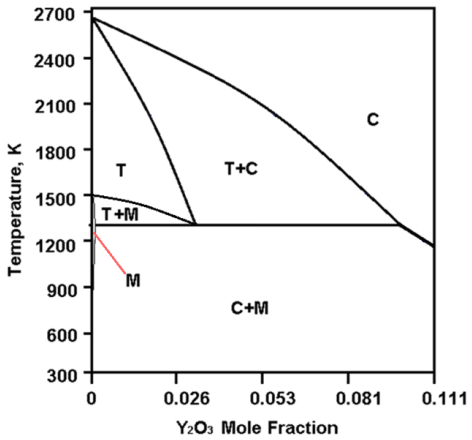

Figure 1. Phase diagram of yttria-stabilized zirconia. C – cubic phase, T – tetragonal phase, M – monoclinic phase.

The dependencies of oxygen diffusion coefficients on yttria content for cubic and tetragonal YSZ were essentially similar (Figure 2).

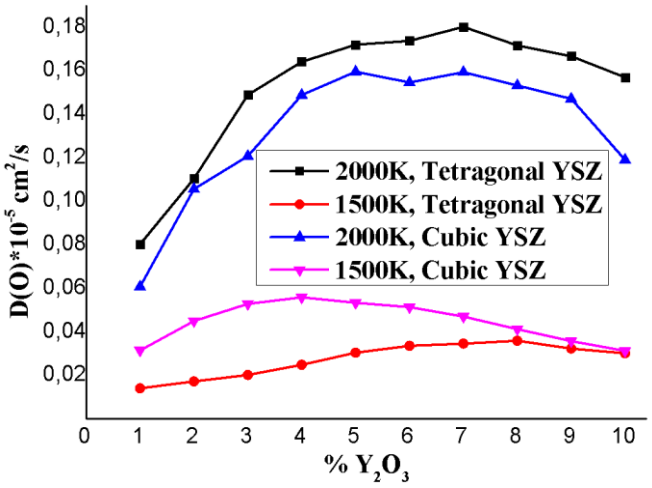

Figure 2. Diffusion coefficients for tetragonal and cubic YSZ at two different temperatures (1500K and 2000K).

The phase diagram-based approach used in the present work for evaluating the conductivity of heterogeneous YSZ samples demonstrated a significant improvement over single-phase predictions (Figure 3). As a result, we were able to reproduce the available experimental data and to provide a molecular-level insight into the phenomena observed in experimental studies.

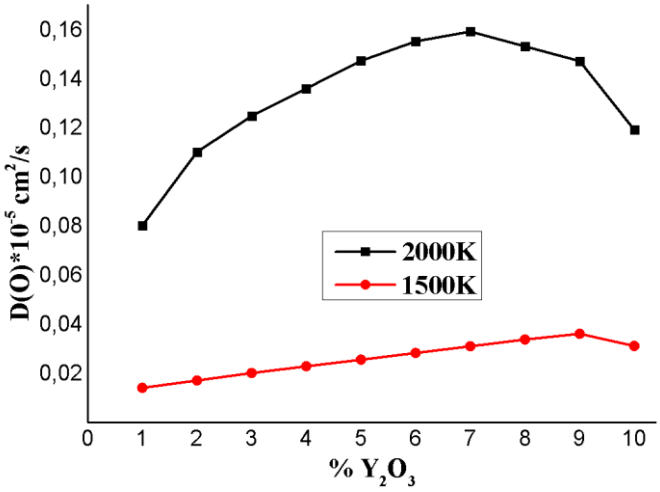

Figure 3. Recalculated values of diffusion coefficients.

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