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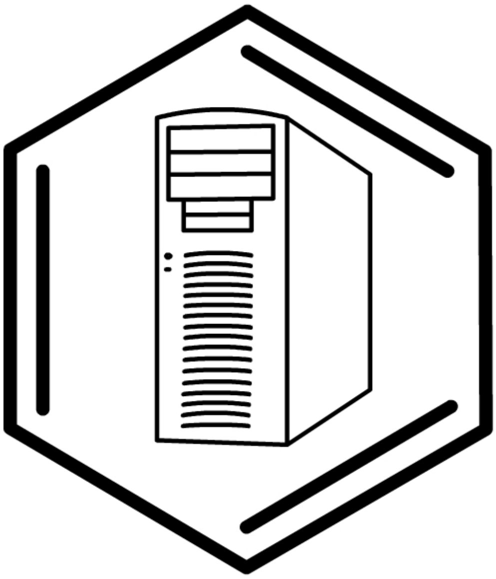
TECHNOLOGY PARK "INSTITUTE FOR SINGLE CRYSTALS"

UKRAINIAN-AMERICAN LABORATORY OF COMPUTATIONAL CHEMISTRY



BOOK OF ABSTRACTS

Methods and Applications of Computational Chemistry

1st International Symposium

Kharkiv, 30 June – 1 July 2005

Kharkiv 2005

Methods and Applications of Computational Chemistry

1st International Symposium

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State-of-the-arts in the electron affinities calculations. Clusters of alkaline-earth elements

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If in atoms only one type of the electron affinity (EA = E_0 (N+1) – E_0 (N)) can be defined, in molecules there are three types of EAs: the vertical electron affinity (VEA), adiabatic electron affinity (AEA), and vertical electron detachment energy (VEDE). For reliable calculation of EAs, the employment of high-level electron correlation methods are needed, for instance, the employment of the DFT approaches, even with the modern hybrid potentials, can lead to qualitatively wrong conclusions. The basis sets used for anion calculations have to contain diffuse functions with high angular momenta in order to describe the binding of remote excess electron. They also have to be flexible enough to describe large relaxation upon electron attachment. The Dunning-type augmented correlation consistent aug-cc-pVXZ basis sets with X = T, Q, etc. can be recommended.

The study of binding of an excess electron to clusters of alkaline-earth elements is interesting as an instructive example of unusual properties of complexes of atoms possessing closed electron shells. In Refs [1-3] all three types of EAs of the Be_n and Mg_n (n = 2-4) clusters were calculated at different levels of theory using the aug-cc-pVQZ basis sets. EAs of Be_2 and Be_3 were calculated up to the complete CCSDT level [1]. This benchmark calculation shows that the MP4(SDTQ) results overestimate and CCSD(T) approach slightly underestimates the magnitude of EA, whereas the global minimum in the potential energy surface becomes deeper with a greater accounting of the correlation energy in the row: MP4(SDTQ), CCSD(T), AND CCSDT . The obtained values of VEDE for all studied clusters are large enough to be observed with standard photodetachment technique. The decomposition of VEDE into three components (Koopmans, relaxation, and correlation) and the atomic orbital population analysis at the NBO level are used to elucidate the nature of the outer electron binding in studied anions.

1. I.G. Kaplan, O. Dolgounitcheva, J.D. Watts, and J.V. Ortiz, J. Chem. Phys. **117**, 3687 (2002) .
2. I.G. Kaplan and C.C. Diaz, Int. J. Quant. Chem. **104**, No. 4 (2005)
3. C.C. Diaz, I.G. Kaplan, and S. Roszak, J. Mol. Modeling, to appear (2005).

Optimized strictly localized bond orbitals for hybrid QM/MM method

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Nowadays, methods that combined both quantum mechanics (QM) and molecular mechanics (MM) to study macromolecular systems are well-established. Some years ago we have developed such a method[1,2]. Instead of using the usual link atom approach to saturate the artificial valences of the QM part, we chose to represent the bond connecting the QM subsystem to the MM one by a strictly localized bond orbital (SLBO). These SLBOs are user defined and are considered a constant of the problem, *i.e.* they are fixed (frozen). The traditional SCF procedure had to be modified to take into account that some predefined orbitals were known and frozen. The modified procedure is called LSCF for local SCF.

In this lecture we will give details concerning the LSCF method and its applications to chemical reactivity. In addition, we will present a modification of the LSCF method to take into account the response of the SLBO to the wave function variations and some illustrative calculations will be shown and discussed.

[1] X. Assfeld and J.-L. Rivail, *Chem. Phys. Lett.* **263** (1996) 100.
[2] N. Ferré, X. Assfeld and J.-L. Rivail, *J. Comp. Chem.* **23** (2002) 610.

Polar solvation and electron transfer: from continuum models to molecular simulations

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Treatment of polar solvation effects in the framework of continuum solvent models is widely accepted in theoretical chemistry. This approach allows, in a combination with a quantum-chemical computation of the solute electronic structure, to consider at a semi-quantitative level the effect of polar medium on reaction rates of charged and strongly polar reactants. Advanced theories of this sort include nonequilibrium solvation phenomena by introducing collective solvent coordinates for studying kinetics and mechanisms of charge transfer reactions. Electron transfer (ET) is especially important in this context as a simplest process in which nonequilibrium solvation effects are revealed in the most pure form.

We'll discuss applications of this approach for computing basic kinetic parameters of the ET with main focus on the solvent reorganization energy. The linear response approximation is most important in this context. Being originally formulated within a dielectric continuum model, it can be readily extended to cover microscopic level treatments of a solvent based on molecular simulations. Perspectives of such extension will be discussed and illustrated by recent computations of intramolecular ET in large organic substrates in water and other solvents of different polatity. The scope of validity of continuum models will be considered with several examples explicitly demonstrating their limitations.

Structural forms of two-valent metal cation stabilization in high-silica zeolite. The possibility of appearing of unusually active sites. Cluster model DFT study

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Various forms of two-valent metal cation stabilization in high-silica zeolites are considered on the example of ZnZSM-5 zeolite. Systematic cluster model DFT studies clearly show the dependence of the stabilization energy on the distance between two lattice aluminium ions forming cationic position and on the geometry of the cationic position. The larger is the stabilization energy the less is the chemisorption and chemical activity of the cation; it is demonstrated for heterolytic decomposition of ethane molecule on Zn^{2+} active sites. The statistical distribution of aluminium in the lattice of high-silica zeolites makes probable the appearance of structures with distant placing of the two aluminium atoms. Cations, localized on such sites, should be very strong Lewis acids and chemically active. The example of such site is considered for Zn^{2+} stabilized in the zeolite fragment represented by two adjacent five-member rings on the wall of ZSM-5 main channel. DFT calculations of molecular and dissociative adsorption of H_2, CH_4 and C_2H_6 on such sites are in agreement with experimental data. Adsorption of H_2 as well as CH_4 and C_2H_6 by zinc at such sites results in the unusually large red frequency shifts of some stretching vibrations of adsorbed molecules. The proton migration through the zeolite fragment after the H_2 dissociative adsorption is studied and the calculations of dehydrogenation of C_2H_6 to C_2H_4 is performed.

Variational method in Dirac theory: unexpected results and new developments

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An application of the Rayleigh-Ritz variational method to solving the Dirac-Coulomb equation, although resulted in many successful implementations, is far from being trivial and there are still many unresolved questions [1]. One of the main sources of the difficulties, frequently stressed in the literature, is the unboundedness from below of the Dirac Hamiltonian. Another one, usually less appreciated but at least equally important, is the multicomponent structure of the wavefunction. Our aim is to point out differences and similarities between the behavior of the energy functionals in the Dirac and in the Schrödinger theories and to present several approaches in which problems associated with the specificity of the Dirac-Coulomb eigenvalue problem have been successfully solved. In particular, we present an algorithm which secures that the eigenvalues of the Dirac Hamiltonian are lower bounds to the corresponding Rayleigh quotients [2], a relativistic formulation of the Hylleraas-CI method [3] and a surprisingly simple and accurate quasi-relativistic approach [4]. Unexpected properties of a density functional related to the multi-component structure of the wavefunction [5] and the relations between the choice of the representation of the Dirac Hamiltonian in the spinor space and the performance of the variational principle [6] are also briefly discussed.

1. I. P. Grant, J. Phys. B: At. Mol. Phys. **19** (1986) 3187-3205; J. D. Talman, Phys. Rev. Letters **57** (1986) 1091-1094; W. Kutzelnigg, Chem.Phys. **225** (1997) 203-222.
2. G. Pestka, Chem. Phys. Lett. **376** (2003) 659-661; Phys. Scri. **68** (2003) 254-258; Phys. Scri. **69** (2004) 203-207.
3. G. Pestka, H. Tatewaki and J. Karwowski, Phys. Rev. A **70**, (2004) 024501-(1-3).
4. M. Stanke, J. Karwowski and H. Tatewaki, *Kinetically-balanced Dirac equation*, in preparation.
5. J. Karwowski and M. Stanke, Phys. Rev. A **71** (2005) 024501 (1-4).
6. M. Stanke and J. Karwowski, *Dirac-Coulomb equation in non-standard representations*, in Proceedings of QSCP-IX, J. Maruani and S. Wilson, editors, (2005).

Computational techniques for intermolecular potential energy surfaces and quantum dynamics of Van der Waals complexes. State-of-the-art and challenges in perturbation and supermolecular calculations

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Accurate intermolecular interaction potentials between atoms and molecules are of primary importance to understand spectroscopic and collisional properties of weakly bound complexes. In my talk I will give an overview of the state-of-the-art ab initio techniques that can be used with trust to compute reliable interaction potentials. Special attention will be paid to the merits and drawbacks of the perturbation and supermolecular approaches. I will also address the challenges in the field of intermolecular forces such as interactions between species involving open-shell monomers with spacially degenerate ground-state. Finally, an overview of the nearly exact approaches to describe state resolved spectroscopic and collisional experiments will be given. All these issues will be illustrated with some results from the Warsaw group.

What one can gain from high-order density matrices

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An overview of recent results of analysing molecular electronic wavefunctions by reduced density matrices (RDMs) is given. We restrict ourselves with the three following issues: the Weyl-Wigner formulation of exchange effects [1], a general definition and computation of multicenter bond indices [2,3], and a hole-particle description of RDMs closely related with finding the electronic collectivity measures [2,4].

By using the Weyl symbol of permutation operators we show that the squared Wigner function of the Dirac-Fock density matrix naturally appears from the so-called exchange component of 2-RDM in the independent-particle approximation, so the squared Wigner function is a "classical" counterpart of the Wiberg bond index matrix known in quantum chemistry.

In case of singlet states the most general definition of multicenter bond indices can be given if invoking charge RDMs of arbitrary orders examined previously in [5]. It turns out that just irreducible components of these RDMs give rise to specific cumulants expressing correctly high-order fluctuations of atomic charges. A principal issue concerning the bond indices and atomic valences for the states with nonzero spin is discussed. For this problem a use of irreducible components of the high-order spin density matrices given in [5] leads to a consistent definition of the above mentioned characteristics.

Hole-particle formalism is developed for RDMs. High-order hole-particle densities are extracted from the total RDM reffered to arbitrary *N*-electron state vector, and the corresponding occupation numbers of various types are introduced. They allow us to determine certain average hole-hole, particle-particle and holes-particle distances. Concrete examples show how the proposed indices work for analysing different electronic processes such as electron correlation, excitation and molecular dissociation.

1. A.V. Luzanov, O.V. Prezhdo, Int. J. Quant. Chem., **96**, 484 (2004).
2. A.V. Luzanov, Kharkov University Bulletin, 2004, №626, Chemical Series Issue. 11 (33).
3. A.V. Luzanov, O.V. Prezhdo, Int. J. Quant. Chem., **102**, 582 (2005).
4. A.V. Luzanov, O.A. Zhikol, O.V. Prezhdo, this edition, p.
5. A.V. Luzanov, G.E. Whyman, Int. J. Quant. Chem., **20**, 1179 (1981).

Spontaneous mutations in DNA: new support for the old proposal

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Among the techniques successfully applied in investigations of features of different species including large biomolecules, computational methods have increasingly gained popularity. Fast development of hardware and constant improvements in computer coding make high-performance computational techniques a promising alternative to experimental studies. This is especially attractive when experimental data are not available and a theoretical approach could supply information of accuracy matching those of reliable experiments.

DNA components certainly are among the most elaborated biomolecules, and details of their activity are far from being completely understood. Recently computers are routinely applied in such studies, and at least visualization, database, and simple energy minimalization procedures are performed in most experimental laboratories. Nonempirical calculations which employ a high level of theory are alternative sources of information for DNA fragments. *Ab initio* techniques have been in the last few years successfully applied to reveal information concerning their structures and characteristics.

The talk covers the results of recent high level ab initio studies on properties and structures of the DNA bases and their complexes. The discussion will focus on their molecular structures, stabilities, hydrogen bonding, proton transfer and vibrational characteristics. The new evidence of involvement of the rare forms of the bases in the DNA spontaneous mutations will be provided.

DFT cluster model studies of molybdenum based catalysts

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Molybdenum oxide based catalysts are active and selective in many reactions of very different types (selective oxidation, oxidative dehydrogenation, isomerization, polymerization, hydrodesulphurization). The richness of molybdenum chemistry results from many parameters that can vary and which determine the catalytic behavior of molybdenum compounds. One of them is valence state of Mo that can rang from 6+ to 2+, which is directly demonstrated in the case of catalysts composed of pure molybdenum oxide or this oxide deposited on supports. The other one is the Mo local environment; Mo may appear in crystallographic structures in tetrahedral and octahedral coordination and, in addition, may form compounds in which the MoO_3/MO ratio varies. Furthermore, molybdenum oxides can combine with other elements such as Bi, V, Co, or Mn forming a large group of materials (molybdates, molybdenum bronzes, heteropolyacids) that are used as catalysts. Here, coordination of Mo depends on the chemical composition and for the given chemical formula, on radius and electronegativity of M cation. Additionally, various types of atomic defects, reconstructions and rearrangements, which have the implications for surface electronic structure, characterize oxide surfaces. Due to the chemical richness of Mo-O surfaces the various chemisorptions and physisorption interactions exist at the surfaces.

The role of all above-mentioned factors on catalytic properties of the surface is illustrated taking Mo-O-based catalysts as examples. First, the nucleophilic properties of differently coordinated surface oxygen atoms, which are present at pure (010)MoO_3 surface is discussed. In the next step the results of the creation of local mono- and di-vacancy of oxygen type are studied. Moreover, the adsorption of hydrogen that leads to surface hydroxyl and water species is taken into account and the role of such species in the formation of local vacancy is discussed. In addition, process of surface re-oxidation that leads to the formation of very active surface oxygen species is also concerned. Further, metal reduction states (MoO_3, MoO_2) are studied in order to examine their influence on electronic parameters of oxygen sites. The influence of the additional atoms (Mn, Co) on chemical properties of active sites is examined by the comparison of the electronic structure of cobalt and manganese molybdates ($CoMoO_4$, $MnMoO_4$) with the pure Mo-O (MoO_3) system.

The electronic structure is determined by ab initio density functional theory, using StoBe code. Electron exchange and correlation are described by the local (VWN functional) and gradient corrected (RPBE functional) spin density approximations. For all atoms all electron basis set is used whereas the $[Ar]3d^{10}$ core of Mo is approximated by model core potentials. The results are discussed in terms of electronic parameters such as atomic charges, bond orders, total as well as atom projected density of states. The electronic properties of the selected (010)MoO_3, (011)MoO_2, (110)$MnMoO_4$ and (100)β-$CoMoO_4$, surfaces are examined using the cluster approach.

Results of calculations show that in all studied systems, surface oxygen species are characterized by different electronic structures. The substitution of molybdenum atom(s) in the clusters by additive atom(s) changes the local electronic state and, what follows, the local reactivity of different surface oxygen sites (Mo=O and Mo-O-X X=Co, Mn) that are present at the catalyst surface. Total and partial density-of-states (PDOS) curves obtained for the clean and defected MoO_3(010) and for clean MoO_2(011) give a clear picture of the reduction mechanism in Mo-O systems. Theoretical data shows that the creation of oxygen vacancies is connected with considerable relaxation of the surface and in additionally is facilitated by the presence of H, i.e. by the formation of surface OH/H_2O species that can desorb from the surface more easily than surface oxygen.

Integrated Approach to Film Growth Modeling

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An integrated approach to the simulation of dielectric thin-film growth is developed. The approach includes *ab initio* calculations of the main gas-phase and surface reactions (reagents, intermediates, products, transition states) using embedded cluster DFT and periodic slab plane-wave DFT methods, estimation of the rate constants using transition state or RRKM theory, kinetic modeling using the kinetic Monte Carlo (kMC) method or formal chemical kinetics. The kMC method is supplemented with a dynamic relaxation procedure in the cases when it is necessary to model irregular growth (defect or amorphous films). Various levels of this approach are exemplified by chemical vapor deposition (CVD) of silicon nitride from SiH_2Cl_2 and NH_3 and atomic layer deposition of ZrO_2 and HfO_2 from $ZrCl_4$ and H_2O. The difference between ZrO_2 and HfO_2 is analyzed.

From high-level multireference *ab initio* theory to on-the-fly dynamics: the photochemistry of the C=C bond and beyond

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The photochemical properties of π systems are of fundamental importance. A comprehensive, theoretical description encompasses several computational steps starting from the calculation of electronically excited states up to dynamics calculations. The computation of excited-state surfaces is particularly difficult since the required wave functions have a complicated multireference structure and conical intersection will occur, at which the fundament of the Born-Oppenheimer is breaking down. Quantum dynamics calculations are limited to the a few degrees of freedom and usually require the pre-computation of the energy surface. Alternatively, classical on-the-fly surface-hopping dynamics calculations can be performed.

In the present contribution the progress in terms of analytic multireference configuration interaction (MR-CI) gradients and nonadiabatic couplings based on the COLUMBUS program system (http://www.univie.ac.at/columbus/) will be used to discuss the characteristics of the energy surfaces of ethylene and of a selected set of molecules containing polar C=C bonds (silaethylene, fluorethylene and formiminium cation). The latter is of interest since it is the smallest member of protonated Schiff bases. Nonadiabatic surface-hopping dynamics calculations based on the semiempirical AM1 method (including parameter fitting), CASSCF and MR-CISD will be presented.

First results on the dynamics of models for retinal, which is the basic chromophore in the primary process of vision, will be presented.

Computational chemistry methods on molecular magnetism

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Past decades molecular magnetism has been one of the central research areas in molecular science. This is a multidisciplinary field in which experimental physicists, inorganic chemists, organic chemists and theoreticians are involved. In particular, theoretical studies can be of great help for the understanding of the relation between the structure and magnetic properties of known compounds and for predicting the magnetic behavior of new compounds.

The standard way for describing the magnetic behavior of a material is through effective spin Hamiltonians in which the magnetic interaction between two magnetic centers is modeled by only a parameter called magnetic coupling constant, J.

On the molecular magnetism field several models have been developed for a qualitative study of the trends of the magnetic coupling constants [1,2]. An alternative strategy is to adopt a quantitative approach by performing *ab initio* calculations of the magnetic coupling constants, quantity related with the energy difference between the different magnetic states. This approach, however, involves a highly challenging computational problem because in molecular magnetism the energy differences between the different magnetic states are usually smaller than 100 cm^{-1}.

Due to the degree of accuracy required in calculating the difference energy and the localized nature of the magnetic interactions, multiconfigurational calculations on properly embedded cluster models are well suited for these studies. In the past few years, CASSCF/CASPT2 has been proved to be an efficient method for computing the magnetic coupling constants. Near degeneracy correlation can adequately be treated by Complete Active Space Self Consistent Field (CASSCF) calculations, while dynamical electron correlation is accounted for by perturbation theory (CASPT2) [3].

An alternative method for computing the magnetic coupling constants, which can allow the study of large systems, is the Density Functional Theory. Initially, DFT provided very poor estimates of the magnetic coupling constants due to two main reasons. First, the inability of DFT for describing the low spin states and second, the tendency of pure exchange-correlation functionals to overestimate the antiferromagnetic nature of the magnetic interactions. At present, these two problems have been overcome by the combination of the Broken Symmetry method and hybrid exchange-correlation functionals resulting in accurate values of the magnetic coupling constants [4].

1. P. J. Hay, J. C. Thibeault, and R. Hoffmann, J. Am. Chem. Soc. 97, 4884 (1975)
2. O. Kahn and B. J. Briat, J. Chem. Soc. Faraday Trans. 72, 268 (1976)
3. C. de Graaf, L. Hozoi and R. Broer, J. Chem. Phys., 120, 961 (2004)
4. E. Ruiz, J. Cano, S. Alvarez, and P. Alemany, J. Chem. Comp. 20, 1391 (1999).

DFT study of the Pt nanoclusters and the CO sorbtion on them

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Recent studies have shown that properties of nanoclusters and nanoparticles may differ significantly from their solids. Experimental studies of cluster systems are characterized by considerable difficulties. Among them there are formation of clusters with fixed size and shape. Therefore theoretical quantum-mechanical calculations of electronic and space structures of nanoclusters and their properties play important role for heterogeneous catalysis. Quantum-mechanical calculations give information about shape of clusters, their energy formation, and electronic structure of clusters. Moreover theses calculations allow consider an effect of substrate on the properties of clusters.

Using density functional theory (DFT) with gradient-corrected exchange-correlation functionals (B3LYP), we have studied the electronic structure and bonding of CO to various Pt-clusters. Our aim is to understand how the cluster size and shape affect the sorbtion of CO molecule on the various Pt-clusters.

We calculated various Pt_n-clusters for n=1 – 8 to obtain minimum energy structure with a restriction that Pt nanoclusters are characterized by planar structure and single spin state. Fig. 1 presents the dependence between bonding energy of Pt nanocluster and number of atom in nanocluster. Calculations have shown that the bonding energy sharply decreases with increasing number of Pt atoms in nanocluster from 4 to 8.

We have also studied the CO sorbtion on optimized Pt-nanoclusters. It was assumed that optimized Pt-clusters are strongly bonded to substrate and the CO sorbtion does not change geometry of optimized cluster. We calculated equilibrium structures Pt_nCO for n=1 – 7. It was found that the CO molecule prefers to bond with extreme atom of Pt-cluster. Except Pt_2CO, the CO molecule is located on bond Pt–Pt. Fig. 2 shows dependence between bonding energy of CO molecule sorbed on the Pt nanocluster and number of atom in cluster.

Our studies have shown step-like dependence of the energetic and sorption properties of Pt nanoclusters on number Pt atoms in them.

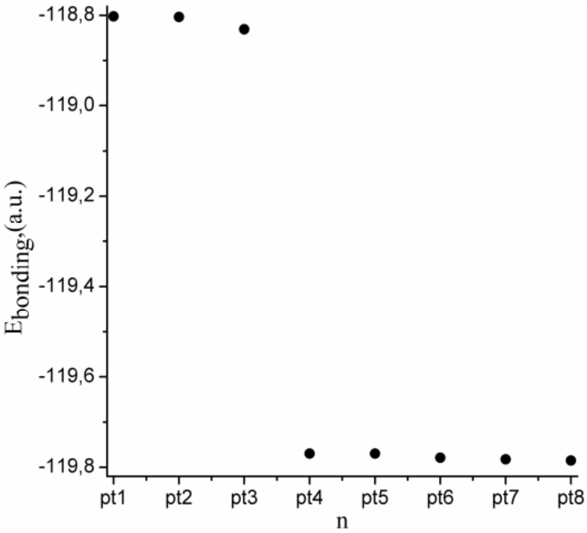

Fig. 1. Dependence bonding energy on number of atoms in the Pt-clusters

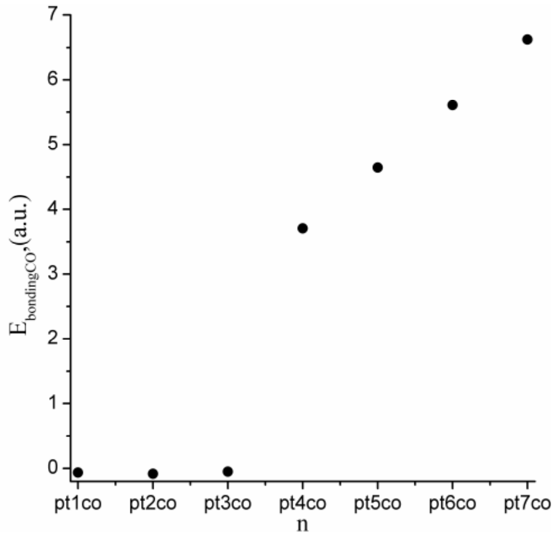

Fig. 2. Dependence bonding energy of CO on number of atoms in the Pt-clusters

Mutagenesis – extensive field of action for specialists in computational chemistry

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At present, the generally accepted explanation of mutagenesis nature rests exclusively upon the idea that it is conditioned by sporadic errors of DNA polymerases. However, such an approach can't explain some phenomena of UV-mutagenesis and contradicts some experimental facts.

A model of ultraviolet mutagenesis has been developed and a basis has been created for studying mutagenesis under the action of free radicals (which are the main cause of spontaneous mutagenesis, mutagenesis under the action of ionizing radiation and partly of chemical mutagenesis). Pyrimidine cyclobutane dimers and (6-4) adducts are main damages under the UV-radiation of DNA molecule. Mutations of all types originate, as a rule, in processes of SOS-synthesis or reparation of damages. Mutations occur most frequently opposite the dimers (the targeted mutagenesis). Sometimes they originate in a small vicinity of dimers (the untargeted mutagenesis).

It has been shown how the UV radiation of DNA molecule can induce changes in the tautomeric state of paired DNA bases. The quantum- mechanical calculations show that for the G-C pair and, possibly, for the A-T pair one of new pairs are in a small vicinity of dimer (10-15 bases) this can be the reason of untargeted mutagenesis.

It is shown that during dimer formation the tautomeric state of component bases may change. As during dimer formation the DNA strand becomes curved and the hydrogen bonds between paired bases are broken, then all the new tautomeric states will be stable. There are 4 new rare tautomeric forms for thymine and adenine molecules and 6 for guanine and cytosine molecules that influence the character of base pairing. A model has been developed for transformation of potential mutations into base substitution mutations during DNA SOS-synthesis.

The model of the mechanism of changes in the tautomeric state of bases induced by the UV radiation rests upon the knowledge of surfaces of the potential energy of paired bases, oscillation frequency of atoms and atomic groups in the DNA as along DNA strand, etc. A list of problems to be solved for studying the nature of UV-mutagenesis is represented.

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Optimization of interelectronic potentials in the extended-Hubbard (PPP) Hamiltonian with the application to fullerene C_{60} electronic spectrum

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Quantum-mechanical calculations of electronic structure of cage carbon clusters, fullerenes and nanotubes, are recognized as important means for deeper understanding of their unique physical properties significant for technological applications. For the carbon clusters of practical interest, essential difficulties in the application of *ab initio* methods arise from the great sizes of systems and from the eventual need to consider nanotubes with translational invariance, broken by defects, edges or bends. Moreover, because of their intrinsic electronic characteristics, carbon clusters are the systems with a strong electron correlation, and therefore, in many cases, the many-electron effects should be treated explicitly. Thus, as it concerns carbon clusters, a valuable alternative to *ab initio* methods are semiempirical approaches, in the first place, various modifications of the extended Hubbard or, that is the same, Pariser–Parr–Pople model. The main problem in their application to carbon clusters is the parametrization of model Hamiltonians, taking into account the specific features of cage cluster such as curvature of the carbon sheet forming a cluster and shape of the screened electron-electron potential. Thus, the parameters of the electron–electron potential should be tested and eventually readjusted to yield an agreement between theoretical predictions and experiment.

This report presents a numerical procedure for the optimization of electron–electron potential in a spatial quasi-pi-electron model and the results of its realization on the example of fullerene C_{60}, the simplest representative of carbon cluster structures. Among the numerous known forms of electron– electron potentials, the Ohno functional form modified by Harigaya and Abe (Phys. Rev. B.49, 16746, 1994) is used here to test tentatively an optimization procedure. In this potential, dielectric screening of the long-distance electron–electron interaction of Coulomb type is introduced via an independent parameter. In this case the Hamiltonian can be scaled, thus only two optimized values persist, the Hubbard one-center parameter determining the magnitude of overall electron– electron interaction, and screening parameter that determines the contribution of long–range interaction. Their values are optimized with respect to consistency of calculated dipole-active transitions with experimental C_{60} absorption spectra. The calculations of mono-photon excited states are performed by the CI method on the set involving about 200 mono-excitations.

A quantitative criterion is proposed that measures deviation of calculated values from proportionality to the experimental ones. Transition energies and oscillator strengths are tabulated on the two-dimensional parameter lattice restricted by physically reasonable parameter values. In the spectroscopic range 2 – 6 eV of absorption spectrum of C_{60} in solution three strong bands and an additional slight low-frequency peak about 3 eV are observed. So theoretical dipole-active excitations can be compared with experimental peak positions along two possibilities, 4-band pattern including 3 eV peak and 3-band pattern ignoring it. The both possibilities have been considered. For each lattice point of tabulation, two criterion values, one for the transition energy and another for the intensity, are calculated. A minimax procedure for compromise parameter choice taking into account relative importance of both spectral characteristics is proposed. The results obtained by its implementation shows that simultaneous consistence of transition energies and intensities is of strongly contradiction character which is the case for both considered patterns of comparison. One can point out the possible directions of yielding better consistency (i) using more suitable functional form of the e–e potential; (b) including double or higher excitations in the CI calculations; (c) modification of one-electron part of the model Hamiltonian. We hope that the proposed optimization procedure would be helpful also in these more complicated cases.

The informational field of molecule as novel viewpoint on chemical structure

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The structure-informational representation of molecules are enough widely used for solving problem "structure-properties". For many topological indexes their informational analogs are constructed. In essence, all of them reflect an amount of information that is contained in the considered molecular model.

In present work we have tried to simulate situation, when the molecules transmit the information about their structure to enclosing space. Actually, the formal model is offered which shows the space becoming inhomogeneous by "entering" into it of the molecular structure. The heterogeneity of space depends on complexity of molecular structure that may be expressed by amount of information. Actually, any field of a molecule is informational.

For modeling an information field of a molecule enough consistently to apply Shannon's approach (probabilistic-statistical conception of the information) not only to investigated object (molecule), but also to space surrounding it.

Let's consider the idealized situation: the "empty" infinite space is divided into identical areas (cells). We have no bits of the information, since all cells are absolutely identical, there is no variety and hence there is no information. But as soon as we place any object in this space, then equivalence of many cells is deleted. Cells become different and their difference depends on observation place of the object. We (receiver - observer) can receive different quantity of the information about this object being in various places of surrounding space. Thus, for modeling field of the potential information in the definite area we should be able to differentiate cells of space surrounding object. When all cells in the definite area of space will be divided on groups, we will need only to apply the Shannon's formula and to calculate the potential information in each cell, in group of cells and in whole area. Generalizing the above stated, the following conclusion is possible:

from a formal position the model of the potential information field of any object describes a situation, when surrounding space is structurized by the object. I.e. object generates the potential information in this area.

What is the reason? A complex of real physical fields of research object can cause structuring of space around itself. However in the given context we do not consider how occurs the structuring of space. We analyze only results. We do not negate physical mechanisms of information transfer from object in surrounding space; we do not concretize them.

The information field of complex object (molecule) is considered as superposition of information fields of its elements (atoms). Using any property of atoms in a molecule, it is possible to build the weighed information fields which will reflect the information on distribution of the given property in space. Such distribution is completely determined by corresponding molecular structure.

Different applied aspects of the informational molecular field are considered, in particular:

- construction of a chirality information field of molecules, reflecting ability of a chiral molecule to dissymmetrize surrounding space, was developed.
- analysis of efficiency of "host - guest" complementary binding the methods of estimation of the complementary of informational fields were offered.
- procedure for a quantitative estimation of structural similarity/ distinction of various organic compounds were created.
- on the basis of informational field parameters different QSAR tasks were solved.

Modeling DNA conformational transformations

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One of the productive ways to understand the conformational resources of DNA macromolecule is the use of phenomenological approach to modeling double helix transformations. Under successful model construction the phenomenological approach allows to describe the structural transformations in macromolecule of the real size and with the account of surrounding factors. It is also important that phenomenological approach makes clear the physical nature of the processes under consideration and then may be amplified by the precise calculations in some principal points.

The approach for description of the DNA conformational transformations in the frame of double-helical state (transitions of *B-A* type, heteronomic and “close – preopened” transformations) is proposed. Basing on the results of the modeling of the conformational vibrations of the double helix and due to the consideration of joint motions of the structural elements on conformational pathways the unifying model for the study of DNA conformational transformations is constructed. For different trajectories of DNA structure transformations the expressions for the macromolecule free energy are obtained in the two-component form. One component of the model is the degree of freedom of the elastic rod and another component – the effective coordinate of the conformational transformation. Both components of the model are interrelated, as it is characteristic for the soft macromolecule structure of the DNA. As shown, the kinetic energy of different type conformational transformations of the heterogeneous DNA may be put in the homogeneous form. At the same time the potential energy remains dependent on the nucleotide sequence and in the case of the description of double helix preopening - on the nucleotide content also.

The comparison of theoretical results with the experimental data on intrinsic DNA deformability shows good qualitative agreement and demonstrates the effectiveness of the proposed approach. The correlation between the macromolecule deformations and the number of the intrinsic conformational excitations is shown.

The important conclusions about the possibility of the existence of localized excitations in DNA macromolecule under natural conditions depend on accuracy of force constants determination. For further progress in this area it will be productive to use the computational methods for precise characterization of the force field of DNA conformational transformations.

S^2-expansion Technique in the Basis of Paired Orbitals

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Wide use of unrestricted density functional theory (UDFT) for various open-shell systems like transition-metal compounds revived the problem of spin-mixture contained in the unrestricted determinant (Ψ^U). Analysis of spin mixture contained in Ψ^U can be in general carried out by using projection technique which is though rarely applied in practice due to its complexity. It appears that such analysis becomes substantially easier if performed in basis of Löwdin-Amos-Hall "paired" or "corresponding" orbitals which are all orthogonal except for m pairs (m is a number of β spins). The orbital space determined by paired orbitals can be naturally divided into the subspaces of completely, partially and non-overlapping orbitals. Then, spin contamination can be associated with the "active" subspace of k partially overlapping paired α and β orbitals with k being fairly small number in practice. In the active subspace Ψ^U is expanded in a linear combination of restricted determinants constructed either from paired or unrestricted natural orbitals. Although such basis determinants are not the spin eigenfunctions having spin contamination $<\mathbf{S}^2\text{-}S_z(S_z+1)>$ equal to 0,1,2,…,k they allow one to obtain a transparent assignment of the effective electron configuration(s) responsible for given unrestricted solution. For instance, non-zero spin contamination is interpreted as a measure of covalency in the bonding of antiferromagnetically-coupled paramagnetic centers.

Why N-methyleneformamide, CH_2=N-CHO, prefers g*auche*-conformation? Density functional and NBO study

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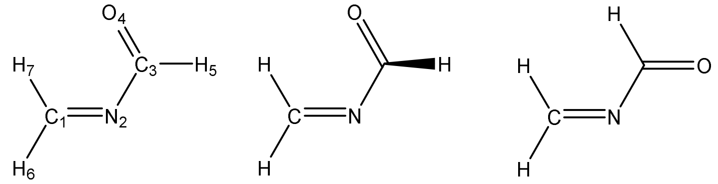
Conjugated diene-type systems are of great importance in the theory of organic chemistry because they have played a key role in the development of basic theoretical models. Recently [1], interesting nitrogen-containing aldehyde, N-methyleneformamide CH_2=N-CHO, was investigated by means of DFT and MP2 methods. It has been suggested that against other similar molecules, N-methyleneformamide was found to exist predominantly in *gauche* conformation, whereas non-planar *gauche* conformations were found to be non-stable transition states in the similar cases. In the present work we have applied Natural Bond Orbital method with the purpose to explain the conformational preference of N-methyleneformamide CH_2=N-CHO, to have a definitive answer about the factors leading this molecule to be non-planar.



cis *gauche* *trans*

Figure 1. Three possible conformations and atom numbering for N-methyleneformamide

All conformers **(Fig. 1)** were fully optimized at the B3LYP/6-311+G(d,p) level of theory using Linux version of PCGAMESS v. 6.5 package. Standard basis set 6-311+G(d,p) has been used as fully adequate for purposes mentioned above and for the better comparability with the results of previous studies. The NBO 4.M program was used as implemented in the PCGAMESS package. Finally, N-methyleneformamide was predicted to exist predominantly in the *gauche* conformation, as has been stated earlier. We found [2] that this preference is due to the strong $\boldsymbol{\pi_{C1\text{-}N2} \leftrightarrow \pi_{C3\text{-}O4}}$ and $\boldsymbol{\sigma_{C3\text{-}H5} \leftrightarrow n_\sigma N2}$ repulsive interactions in the planar *cis* and *trans* geometries, instead of $\boldsymbol{n_\sigma N2 \leftrightarrow n_\sigma O4}$ and $\boldsymbol{n_\sigma N2 \leftrightarrow n_p O4}$ repulsive interactions predicted by Badawi [1]. Higher relative conjugative stabilization, involving lone pair on nitrogen atom, in comparing with the other conformations, also accounting for the greater stability of *gauche* N-methyleneformamide.

1. H. M. Badawi, J. Mol. Struct. (THEOCHEM) 617 (2002) 9.
2. D.Yu. Afanasiev and A.V. Prosyanik, J. Mol. Struct. (THEOCHEM), *xx, (2005) 1-5.*

Ab initio modeling of $C_{36}H_{42}[NV]^-$ and $C_{36}[NV]^-$ nanodiamonds

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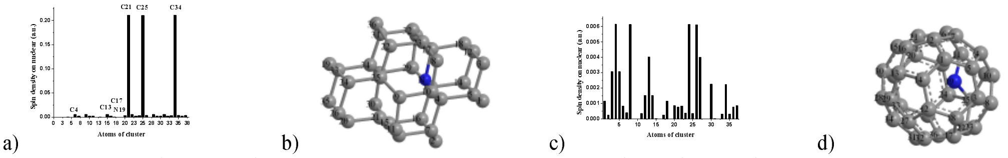
Nowadays the diamond nanocrystals with embedded $[NV]^-$ defect centers are of special scientific and applied interest due to perspectives of their application for quantum computing [1].

The $[NV]^-$ defect centers consist of substitutional nitrogen atom and vacancy in the nearest site of diamond lattice. This negatively charged center have triplet (S=1) ground electronic state. If isotopic ^{13}C atoms are disposed nearby the $[NV]^-$ center then such system of interacting electron and nuclear spins can serve as a prototype of quantum computer [1]. It is important to know the distribution of spin density over various isotopic ^{13}C atoms around $[NV]^-$ center, because, as is well known, the hyperfine coupling of the electron spin of the $[NV]^-$ center to the ^{13}C nuclear spins is proportional to the spin density in positions of such nuclei. Therefore, the main aim of this investigation is to perform quantum-chemical computer simulation of spin properties of $[NV]^-$ center in diamond $C_{36}H_{42}[NV]^-$ and $C_{36}[NV]^-$ – hydrogen passivated and nonpassivated nanocrystals.

Simulations of the nanocrystal properties were performed after complete geometry optimization within semiempirical (PM3) and *ab initio* (using DFT with B3LYP1 potential) quantum-chemical methods. All calculations have been done with software packages PC GAMESS [2] based on GAMESS (US) [3] and CAChe [4].



a) b) c) d)

Fig. 1 a) Spin density distribution histogram over nuclei of the cluster $C_{36}H_{42}[NV]$; b) Geometry of the cluster $C_{36}H_{42}[NV]^-$. Атом N is at position 19, H atoms not represented. c) Spin density distribution histogram on atom nuclei for cluster $C_{36}[NV]^-$; d) Geometry of the $C_{36}[NV]^-$ cluster.

It is shown that for the clusters $C_{36}H_{42}[NV]^-$ containing single $[NV]^-$ center, the spin density is localized basically on carbon atoms being closest to the vacancy. (Fig. 1 a,b).

In the case of $C_{36}[NV]^-$ nanocrystal the spin density is delocalized practically uniformly over the nuclei of C atoms, which form the fullerene-like shell (Fig. 1 c,d).

1. Wrachtrup J., Kilin S.Ya., Nizovtsev A.P. Optics & Spectroscopy. 2001. V. 91. P.429.
2. Granovsky Alex A., WWW http://classic.chem.msu.su/gran/gamess/index.html
3. Schmidt M.W., Baldridge K.K., Boatz J.A. *et al.* J.Comput.Chem. 1993. V.14. P.1347.
4. http://www.cachesoftware.com

Studying of ethylene glycol and glycerol complexes with ions of sodium and chlorine with the methods of quantum chemistry

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The results of *ab initio* quantum-chemical calculations for the complexes of cryoprotector molecules of ethylene glycol and glycerol with ions of sodium and chlorine by MP2/6-311++G** method are presented in this work. Calculations have been performed for an explanation of some features of mass spectra of the solutions containing the specified components. Namely, in the low temperature secondary emission mass spectra of solutions of substances which are sources of ions Na^+ and Cl^- in cryoprotector with an expected series of cryoprotector with cation clusters a series of intensive associates with anion has been registered. Comparable absolute intensity of the associates with Na^+ and Cl^- shows that the stabilization energy of these solvate complexes has very close values.

Problem of study of the interactions of cryoprotectors with the ionic environment in solution has appeared in connection with consideration of cryobiological problem of their influence on bimolecular functioning [1].

As a result of calculations a number of stable configurations of ethylene glycol and glycerol complexes with Na^+ and Cl^- ions in which the ion has one, two or three bonds with a molecule has been received. Energies of the most stable associates are shown in the table.

Energies of interaction of Na^+ and Cl^- ions in the most stable complexes with ethylene glycol and glycerol molecules

	Na^+	**Cl^-**
Energy of interaction with a molecule of ethylene glycol, kJ/mol	-174.6	-109.3
Energy of interaction with a molecule of glycerol, kJ/mol	-190.5	-128.8

Structures with multiple contacts of alcohols with ions appeared more energetically favorable. Geometry of some complexes of ions with glycerol and ethylene glycol appeared to be similar. Comparison of similar anion and cation associates stability depending on the size of alcohol shows that for the ion of sodium it's energetically more favorable to contact with ethylene glycol, and for an ion of chlorine - with glycerol.

It's interesting that for the complex of a sodium ion with glycerol the interaction energy increases with growth of bonds quantity, at the same time for an ion of chlorine the most favorable structure is that with two bonds rather than with three ones.

Comparison of the energies that have been calculated for the solvate complexes of ions Na^+ and Cl^- and polyatomic alcohols with those for hydrated complexes of the same ions with a molecule of water and for complexes of Na^+ ions with some nitrogenous bases of nucleic acids [2] shows that the interactions of cation and anion forming stronger bonds with the alcohol molecule. The stronger bonding of the cation and anion with a cryoprotector molecule can be of interest in cryobiology for an estimation of the mechanisms of cryoprotector action at a molecular level.

The results of quantum-chemical calculations showing sufficiently high stability of complexes of ions of both Na^+ and Cl^- with a molecule of alcohol allowed to explain high and comparable peak intensity of the complexes under consideration which have been registered in secondary ion mass-spectra.

1. Pushkar N.S., Shargo M.I., Belous A.M., Kalugin Yu.V. Cryoprotectors. Kyiv:Naukova dumka. 1978. 204p.
2. Schalley Ch.A. Mass Spectrom. Reviews. 2003. V. 20. P. 253-309.

On the thermodynamics of Heisenberg-Ising spin-1/2 two-leg ladder

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In recent years low-dimensional magnetic systems like spin ladders are subject of extensive experimental and theoretical interest because magnetic properties of several classes of materials like $SrCu_2O_3$, $La_6Ca_8Cu_{24}O_{41}$ and $(C_5H_{12}N)_2CuBr_4$ [1,2] can be well described by the two-leg Heisenberg antiferromagnetic ladder model. Due to large quantum fluctuations in low dimensions, such systems often have unusual properties. Unexpectedly big finite-size effects in anisotropic spin ladder systems may be of interest in context of the theory of nanoscale materials.

We propose anisotropic spin ladder model formed by N rungs with uniaxial anisotropic spin coupling and Ising rung-rung interaction. The Ising interaction between rungs leaves z-projection of the spin M_i of each rung ($M_i = 0, \pm 1$), unchanged. Therefore total 2^{2N} dimensional space of all ladder states consists of subspaces with given z-projection of the ladder total spin M. The ladder Hamiltonian has no matrix elements between states in different M-subspaces. Therefore it can be diagonalized separately in each subspace. Because of this feature of the exact energy spectrum, it can be found analytically by means of Jordan-Wigner transformation similar to nearest-neighbor spin chain with alternative Heisenberg and Ising interactions [3]. It is also shown that this spectrum gives the exact lower boundaries for the eigenvalues of the corresponding isotropic Heisenberg spin ladder.

We derived an effective numerical algorithm for the evaluation of free energy of finite clusters of the ladder. For infinite ladder the evaluation of the exact partition function is a complicate combinatorial problem and we did not find the corresponding analytical formula. Nevertheless, our numerical approach is a good alternative to the exact diagonalization study because of bigger size of the corresponding ladder clusters. Numerical simulation has shown up to three maxima in temperature dependence of ladder heat capacity at zero magnetic field.

1. Dagotto E. and Rice T. M. 1996 Science **271** 618
2. Hirikava T. and Furusaki A. 2001 Phys.Rev B **63** 143438
3. Lieb E.H. Schultz T. and Mattis D. 1961 Ann. Phys. **3** 407

The study of the organic compounds electronic structure by the natural bond orbital method. 2. Interaction of the $S(O)CY_3$ and SO_2CY_3 (Y = H or F) functional groups with aromatic ring, double and triple bonds

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The compounds possessing general formula $C_6H_5XCY_3$, $H_2C{=}CHXCY_3$ and $HC{\equiv}CXCY_3$, where: X = SO or SO_2, Y = H or F have been studied by the nonempirical quantum-chemical method at the MP2 (full)/6-31+G(d) approximation. The analysis of the surface potential energy was carried out. The vibration tasks solution enabled to determine the nature of stationary points and evaluate the barriers of fragments internal rotation about the C_{sp^2}–X bonds. It was found that the spatial structures with an approximately perpendicular disposition of the S–CY_3 bonds relative to the benzene ring plane or double bond are correspond to energy-favourable conformations. The value of the rotation barriers about the C_{sp^2}–S bonds exceeds the *kT*. According to the NBO model the S atom of the SO and SO_2 groups of discussed compounds is bound to the O atom by strongly polarized covalent σ-bond ($S^{\delta+}$–O^{δ}). The π-bond electronic density is mainly localized on the O atom too. By the formalism of the NBO-analysis this fact corresponds to three lone electron pairs (LEP) availability on each of the O atoms. The hybrid natural orbital of one LEP (n_σ) has approximately 76 - 80 % s-character while two others LEP (n_{π^1} and n_{π^2}) are practically "pure" *p*-orbitals. For sulfoxides the LEP of the S atom is a hybrid orbital with s-component quota from 50 up to 55 %. The $n_\sigma(O)$ and *n*(S) hybrid orbitals weakly interact with ambient fragments through the donor-acceptor mechanism. Nevertheless the $n_\pi(O)$ LEP effectively interacts with antibonding σ*-orbitals of the adjacent S-C bonds through the $n_\pi(O) \rightarrow \sigma^*(S–C_{sp^2})$, $n_\pi(O) \rightarrow \sigma^*(S–C_{sp^3})$ and $n_\pi(O) \rightarrow \sigma^*(S–C_{sp})$ mechanisms of hyperconjugation. The $n_\pi(O) \rightarrow \sigma^*(S–C_{sp^3})$ interactions are more effective with σ*-orbitals of the C–F bond of the CF_3 group as compared with σ*-orbitals of the C–H bond of the CH_3 group. For sulphones there are additional bonding mechanisms: $n_\pi(O^1) \rightarrow \sigma^*(S–O^{2}{}_{3})$ and $n_\pi(O^2) \rightarrow \sigma^*(S–O^1)$. The electronic structure of the $SOCY_3$ and SO_2CY_3 groups, length, strength and multiplicity of the S–O bonds were mainly stabilized by the hyperconjugational interactions. The donor-acceptor interactions of the *n* (O) with *d*-type Rydberg orbitals of the S atom were less effective. The energies, populations and dipole moments of the natural bonding and not bonding orbitals were analyzed. The total charge on atoms of unsaturated fragments decreases with magnification of the total charge on atoms of the $SOCY_3$ and SO_2CY_3 functional groups. Therefore at identical X (SO or SO_2) the XCF_3 groups possess the stronger acceptor properties as against XCH_3 groups. The electronic density of an aromatic fragment, double and triple bonds is polarized towards the SO and SO_2 groups (according to natural charges values on atoms). There was excess of the electronic density on the C^{ipso} atoms of a benzene ring and C^α atoms of the ethylene and acetylene fragments. Whereas on the C^α atoms of a benzene ring and C^β terminal atoms of ethylene and acetylene fragments - electronic density deficit was observed as compared with a charge on atoms of carbon for unsubstituted benzene, ethylene or acetylene, accordingly.

Ab initio studies of the DNA rare base pairs

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Gas-phase gradient optimization of the DNA rare base pairs containing the lactim forms of guanine (G*) and thymine (T*) as well as the imino forms of cytosine (C*) and adenine (A*) tautomers were carried out using the Hartree-Fock (HF), Density Functional theory (DFT) and the second-order Møller-Plesset perturbation (MP2) methods at the 6-31G(d,p) basis set. It is shown that full geometry optimization at the MP2 level leads to an intrinsically nonplanar propeller-twisted and buckled geometry of the G*-T and G-T* base pairs. The nonplanarity of these pairs is caused by the pyramidalization of the amino nitrogen atoms, which is underestimated by the HF and DFT methods. Hessian calculations at the MP2/6-31G(d,p) level were performed for the optimized geometry of the rare base pairs in order to verify a nature of the stationary points obtained. Inspection of the harmonic frequencies for normal vibrations of nonplanar rare base pair showed only real vibrational wavenumbers for all base pairs. Therefore these optimized nonplanar structures represent energy minimum geometries on the MP2/6-31G(d,p) potential energy surfaces of the rare base pairs. The comparison of the formation energies for the rare base pairs shows the energetical preference of the G*-T and A-C* base pairs as compared with the G-T* and A*-C ones, respectively. It was confirmed from the MP2 calculations that the stabilization energies of the G-T* and A*-C base pairs describing the interaction between monomers are essentially larger than those of the G*-T and A-C* ones, respectively. Analysis of the decompositions for molecular HF interaction energies by Morokuma-Kitaura and the Reduced Variational Space methods showed that the nature of larger stability of the G-T* and A*-C base pairs as compared to the G*-T and A-C* ones, respectively is due to the electrostatic interactions by the 35-46 %. The polarization E^{PL} and charge transfer E^{CT} energies are also 43-71 % larger for the A*-C and G-T* base pairs. It should be emphasized that the correlation interaction E^{COR} makes noticeably larger contribution to the stability of the G*-T and A-C* base pairs than to that of the G-T* and A*-C ones. Thus the larger stability of the G-T* and A*-C base pairs is not related to the correlation interaction. For the better understanding of the question under discussion we have performed the study of the atomic charges for the rare base pairs. The charge assignments of the geometry-optimized structures were derived from the Mulliken population analysis and the electrostatic potential using the Merz–Kollman–Singh scheme. The calculated charges on the proton donor and proton acceptor atoms of hydrogen bonds as well as on their hydrogen atoms of these base pairs showed that the Mulliken charges on the appointed atoms in the G-T* and A*-C base pairs are slightly more electronegative as compared with those of the G*-T and A-C* ones. It can serves as evidence of the fact that the hydrogen bonds in the first two base pairs are more stable by comparison with those in the second ones. The Merz-Kollman atomic charges show that the differences between corresponding charges on the atoms forming the hydrogen bonds for the stereoisomers are else larger. Such a charge distribution on the atoms of the hydrogen bonds can be main reason of the larger stabilization energy for the G-T* and A*-C base pairs than the G*-T and A-C* ones, respectively. According to the energetical point of view the formation of the G*-T and A-C* base pairs must leads to the spontaneous mutations more often by comparison with the G-T* and A*-C ones.

Distribution of electrostatic potential inside arm-chair and zigzag carbon nanotubes

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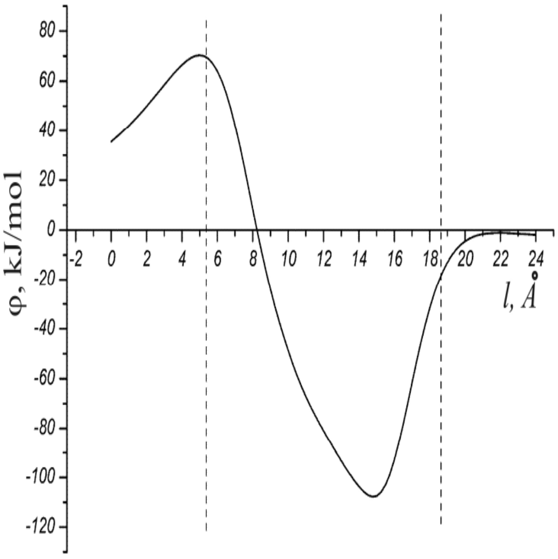
The symmetry of equilibrium configuration of single wall carbon nanotubes (SWNT) is determined by chirality indices (CI) as it follows from semiempirical PM3 calculations. Thus, for “armchair”-type SWNT with CI of (6, 6) a symmetric configuration with C-C bond lengths changing regularly from the periphery to center has an energy minimum. The “zig-zag”-type carbon nanotube with Ci of (8, 0) has a non-symmetric equilibrium configuration. A deviation from the nanotube nuclear core configuration results in non-equivalence of the charge distribution and in different properties of the nanotube ports. It is reflected in the most obvious way via the molecular electrostatic potential distribution ρ calculated by ab initio method within the 3-21G basis set.

The distribution ρ along nanotubes axis has a particular interest. It is shown in Fig. 1a, that there is an extensive region of constant negative ρ values in the central part of “armchair”-type carbon nanotube where a localization is possible of cations or molecules bearing proton donor sites.

The minimum ρ value is practically independent on the tube length (l). The insertion of a probe positive charge into the tube is connected with overcoming a potential barrier of ~ 18 kJ/mol.



a *b*

Fig. 1. A ρ distribution along cylinder axis of SWNT. The dashed lines depict the nanotube ports: *a*- “armchair”-type configuration, *b* - “zigzag”-type one.

A quite different situation is observed in case of the “zigzag”-type SWNT where the change in ρ value along the cylinder axis reflects obviously the non-equivalence of the tube ports (Fig. 1b). The potential minimum is localized near one of the ports. Its value depends on nanotube length. The stronger ρ dependence on l near the minimum as compared with an analogous one for the “armchair”-type tube controls a rigid localization of the cation near one of the ports. The cation entering into the inner cavity via this port is out of barrier whereas the exit of it from another one meets a barrier of 72 kJ/mol.

Structure of singlet and triplet excited states of phothochromic bycyclic aziridines

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Bicyclic aziridines represent a very interesting class of organic compounds, possessing unique photochromic properties. It has been demonstrated that these compounds form deeply colored, fairly stable materials under UV radiation. However, molecular mechanism of photochromism of bicyclic aziridines remains unclear.

Theoretical calculations of bicyclic aziridines **1** (a-f) in ground and excited states were carried out using the TD DFT and CASSCF methods with aug-cc-pvdz basis set.

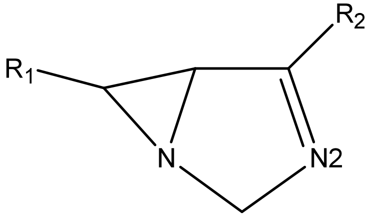

Fig.1. a) R_1=R_2=H, b) R_1=Ph, R_2=H, c)R_1=H, R_2=Ph, d) R_1=R_2=Ph, e)R_1=PhNO2, R_2=Ph, f) R_1=PhOMe, R_2=Ph

The electronic spectra of bicyclyc aziridines were obtained from TD DFT and CASSCF methods. Comparisons of experimental and theoretical spectrum for compound 1e demonstrate reasonable agreement. It has found that triplet excited states have lower value of energy than singlet states.

Molecular geometries of the bicyclyc aziridines in ground and lowest triplet and singlet states were optimized using B3LYP, BHandH, MP2, CASSCF methods and aug-cc-pvdz basis set. The imidazoline ring has a much flattened envelope conformation in ground and singlet excited states. The deviation of the N(2) atom from the mean plane of the remaining ring atoms is 0.09 Å. Such conformation of the five-membered ring results in a slight twisting of the C=N double bond, the C3—N2=C2—C1 torsion angle being 2-4°. Some shortening of the C= N double bond up to 1.278Å (average value is 1.313Å) is observed in ground state. Transition to singlet excited state is accompanied significant further shortening of the C=N bond.

In triplet excited state the imidazoline ring has envelope conformation. The deviation of atom N(2) from the mean plane of the remaining ring atoms is 0.41 Å. Elongation of double bond up to 1.451Å takes place.

For all states the aziridine and imidazoline rings are cis-fused. The angle between the two ring planes is 113°.

The break of three-member cycle is observed for R_1=Ph in triplet and singlet excited sates, that gives rise to formation of a new molecule with utterly different characteristics. In other molecules the break of three-member cycle is not observed. It is characteristic conformation as it is described above.

Computational study of structure-activity relationships for β-lactam antibiotics against PBP5 and inhibitors design

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Bacterial Penicillin Binding proteins (PBPs) are members of the penicilloyl serine transferase family of enzymes [1]. PBPs catalyze the essential reactions in the biosynthesis of cell wall peptidoglycan from glycopeptides precursors [2]. β-Lactam antibiotics inactivate PBPs and interfere with the process of transpeptidation by forming an ester bond between the active site serine and the carbonyl carbon of β-lactam. Based on PBP5 wild type and drug-resistant mutant structures, computational study was carried out to understand the kinetics of this interaction. Structure-activity relationships study shows that the rate of formation of the acyl-enzyme is an essential factor determining the efficacy of a β-lactam, and suggests that the specific side chain interactions of β-lactams could be modified to improve inactivation of resistant PBPs.

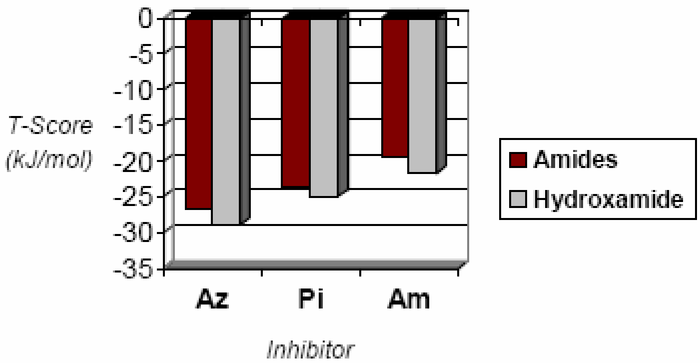
The binding modes and affinities of various β-lactams were predicted by multiple computational modeling approaches. The results fully agree with the experimental data (Table 1).

Table 1 β-lactams inhibitions to PBP5

Inhibitors	IC50 / μM	Ki / μM	T-core / kJ·mol-1	C-score
Azlocillin	25	7+0.3	-26.6	4
Pipercillin	80	36+3	-23.6	4
Ampicillin	125	51+10	-19.4	4

The inhibitor structures were built and minimized energetically with program Sybyl. FlexX [7] was used for flexible inhibitors docking to the wild type protein structure (1NZO in PDB). Relative binding affinities of different inhibitors were inferred by their binding free energy and consensus scores (C-score) [3]. GOLD [4] was chosen to study ligand-binding mode in the flexible protein active site.

Figure1 Hydroxamide Inhibitors Improved Binding Affinity Chart



Hydroxamide inhibitors were designed based on the binding site structure, showing higher binding affinity (Figure 1). More important interactions form between ligand and protein.

1. Ghuysen, J. M. M TrendsMicrobiol, 1994, 2:372-380.
2. Hujer, A. M. et al. Antimicrobial Agents and Chemotherapy, 2005, 49 (2): 612-618.
3. Clark, R. D. et al. J. Mol. Graphics and Modelling, 2002, 20: 281-295.
4. Jones, G. et al. J. Mol. Biol., 1997, 267: 727-748.

Optimized effective potential method and its exchange-only implementation for excited states of molecules

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It is known that a central problem in density functional theory (DFT) is the construction of assumed forms for the exchange-correlation potentials. In view of the fact that the exchange energy is much larger than the correlation one many efforts were focused on the exact treatment of the exchange energy and construction of the corresponding potential. In the ground state theory the exchange potential can be determined using optimized effective potential (OEP) method [1, 2], which, at present, has been recognized as the exact implementation of exchange-only DFT. Unlike the Hartree-Fock (HF) approximation in the OEP method an additional constraint is imposed into the variational problem : the orbitals $\{\varphi_i\}$ must satisfy a single-particle Schrodinger equation with the same effective potential $V_{eff}(\mathbf{r})$ for all the electrons (with the same spin). Then the expectation value of the Hamiltonian with a Slater determinant constructed from orbitals $\{\varphi_i\}$becomes a functional $E\{\varphi_i ; V_{eff}(\mathbf{r})\}$ of such a potential , i.e. the effective potential is varied to minimize the total energy. This leads to an integral equation for $V_{eff}(\mathbf{r})$ whose solution involves the rather large computational efforts. In the last years different methodologies that simplify this problem have been proposed. Their applications to the *ground* state energies of atoms and simple molecules showed that the OEP method performs better than do X-α and conventional Kohn-Sham exchange-only calculations.

For the excited state (ES) calculations the OEP experience is less satisfactory, especially for ESs, having the same symmetry as the ground state. The main applications here have been made for *atoms* within the framework of the ensemble DFT based on an extended Rayleigh-Ritz variational principle, first used in the foundation of DFT for ESs by A.Theophilou [3].

In this communication we present an OEP approach *for individual* non-degenerate ESs based on a simple to implement method of taking the orthogonality constraints into account [4], which was proved to be a useful tool for HF excited state calculations. A variational principle for the functional $E\{\varphi_i ; V_{eff}(\mathbf{r})\}$ subject to some constraints is employed to obtain the OEP integral equations determining optimal $V_{eff}(\mathbf{r})$ for the ES under consideration. A parameterized form of effective potentials expressed in terms of external potential [5] is discussed to simplify a solution of OEP integral equations. A comparison of ES energies for atoms and the HeH molecule computed with the HF , OEP and configuration interaction (CI) method has been made to examine a performance of the proposed approach (see Table, where ES calculations are given for HeH).

Total excited state energies (a.u.) for the HeH molecule at R = 1.5 a.u.

State	OEP	HF	CI	$(E^{OEP}-E^{CI})/E^{CI}$ (%)	$\langle\Phi^{OEP}\mid\Phi^{HF}\rangle$
A $^2\Sigma^+$	-3.065 151	-3.067 422	--3..112 706	1.5	0.998 910
C $^2\Sigma^+$	-3.015 238	-3.015 781	-3.055 797	1.3	0.999 722
D $^2\Sigma^+$	-2.985 067	-2.985 384	-3.030 025	1.5	0.999 825

1.Sharp R.T., Horton G.K.// Phys.Rev. 1953. V.90. P. 317.
2.Talman J.D., Shadwick W.F. // Phys.Rev.A. 1976. V.14. P.36.
3.Theophilou A.K.// J.Phys. C 1979. V. 12. P. 5419.
4.Glushkov .V.N., J.Math.Chem. 2002. V.31. P.91.
5.Theophilou A.K. Glushkov V.N. // Abst. of VIII European Workshop on Quantum Systems in Chemistry and Physics, Spetses, Greece. 2003.

Direct optimization of effective potential for molecules expressed in terms of the electron-nuclear interaction

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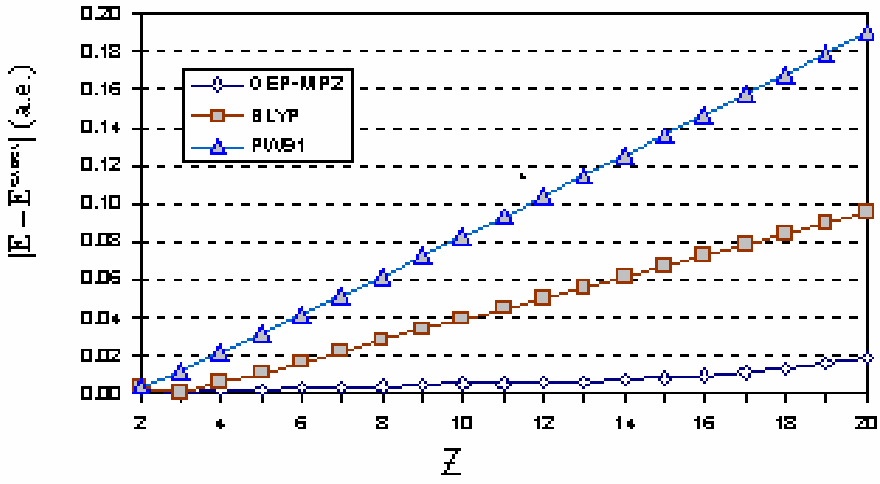
The possibility of reducing the number of variables essential for solving a physical problem is always attractive from both fundamental and computational points of view. Density functional theory (DFT) can serve as an example. In this theory, instead of a wave function (which for a system of N particles is a function of 3N spatial variables), electronic density $\rho(\mathbf{r})$, which is a function of only three space variables, is used as the fundamental characteristic. Although a basis of the theory was established relatively recently, it has become one of the most popular tools in modern electronic structure studies of atoms, molecules and solids. The major problem in DFT is the construction of suitable approximation for the exchange-correlation potential V_{xc}, which in the conventional version are considered as a functional of electronic density, i.e. $V_{xc}[\rho(\mathbf{r})]$. In the course of the development of DFT distinct levels of approximations for V_{xc} can be distinguished. The most promising level in the search of a systematic improvement of energy functional is the use of orbital-dependent representations where V_{xc} is expressed in terms of Kohn-Sham (KS) orbitals. In this case, a problem how to generate the exchange-only potentials is resolved by the optimized effective potential (OEP) method. However the applications of the OEP method is hindered by the computational difficulties posed by the integral OEP equations. Moreover, at present it is not clear what correlation potential can serve as an adequate counterpart of the OEP exchange.

In this communication an alternative methodology that simplifies greatly these problems is developed. This is based on representation of V_{xc} in terms of the electron-nuclear interaction potential $U_{ext}(\mathbf{r})$ [1], i.e. $V_{xc} = V_{xc}[U_{ext}(\mathbf{r})]$. Unlike the conventional DFT such a representation preserves symmetry properties of the external potential and avoids iterative solving the KS equations. At first stage we use the OEP methodology to determine variational parameters of the exchange-only part of effective potential. At the second stage the orbitals and orbital energies determined by solving the KS equations with this potential are used to compute the correlation corrections to the energy according the second-order Moller-Plesset (MP2) perturbation theory. A performance of the proposed technique is demonstrated by calculations of exchange-only and correlation energies (OEP-MP2) of atoms and diatomic molecules and their comparison with the results of conventional DFT (BLYP and PW91 potentials). Some of them are given in Figure.

Energy differences | E–E ^{exact} | for the helium isoelectronic series as a function of atomic number Z



1. Theophilou A.K. Glushkov V.N. // Abst. of VIII European Workshop on Quantum Systems in Chemistry and Physics, Spetses, Greece. 2003.

Structure of variationally-optimized spherical Gaussian basis sets for high precisional energy calculations of molecules

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One of the most important approximations inherent in essentially all standard ab initio calculations is the introduction of a finite one-particle basis set. The incompleteness of such a basis set is currently unavoidable, and the convergence of the energy and other molecular properties with the size of the basis is a critical issue. The problems of construction of the one-particle basis sets have been attracting much attention for about 50 years up to now. The most widely used basis sets in atomic and molecular electronic structure studies are constructed as linear combinations of primitive Gaussian type functions. The quality of such basis sets depends on nonlinear parameters specifying the Gaussian primitives, i.e. their orbital exponents ς_i and positions. The analysis of the variationally-optimized *atomic* basis sets has revealed that sequences of the optimal exponents can be represented approximately by geometrical series defined by only two parameters (so-called even-tempered basis sets) [1]. Applications of such basis sets provided accurate results for *atoms*. However, the Gaussian methodology *for molecules* is still less advanced and needs further development. The most molecular basis sets common use today are *atom-centered* and invariably constructed from atomic basis sets. They have been tabulated and included in contemporary packages of ab initio computer programs. However these basis sets are not optimal for molecules. If high precision must be achieved with atom-centered functions, one needs to use functions of a high angular momentum. It is difficult to achieve sub-μhartree accuracy using even very large atom-centered basis sets. For example, the basis sets as large as aug-cc-pV6Z, consisting of 372 s, p, d, f, g and h functions yields for the simplest molecular system H_2^+ the energy charged with an error of > 1μhartree.

Alternative approach to construction of molecular basis sets is to use so-called *distributed* basis sets where functions are placed potentially over the whole molecule not necessarily on the nuclei. The have been introduced to provide the same effects as the addition of polarization functions, but at a considerably lower cost. A central problem in this approach is in deciding where the functions should be centered.

In the previous papers [2] the variationally optimized basis sets capable of supporting a sub-μhartree accuracy for diatomic hydrides were obtained. In the present study they are investigated with a view to developing empirical schemes for constructing distributed Gaussian basis sets. A careful analysis of such basis sets has been performed and the simple generating rules for the sequences of the exponents and positions of molecules, different from those developed by other authors, have been proposed. In particular it has been shown that the optimal positions r_{iA} of basis functions that are localized around the nucleus A can be generated according to the following prescription

$$r_{iA} = R_A + (-1)^i Z_B \, \delta / \zeta_i , \quad i = 1,2,\ldots,m \qquad (1)$$

whereas known electric-field-variant (EFV) [3] leads to a dependence $r_{iA} \sim \delta / \zeta_i^2$.

A comparison of the ground state energies computed using the fully optimized basis sets, Eq.(1) and EFV relation showed a good performance of the proposed generating rules.

1. Schmidt M.W., Rudenberg K. // J.Chem.Phys. 1979. V.71. P.3951
2. Glushkov V.N., Wilson S. // Int.J.Quant.Chem. 2002. V.89. P.237; *ibid:* 2004. V.99. P.903
3. Sadlej A.J. // Chem.Phys.Lett. 1977. V.47. P.50

Modeling and numerical calculation of complicated enzyme-catalysed reactions

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As is well known life exists owing to aggregate of chemical reaction realized by specific catalysts of protein nature – by enzymes. They provide high reaction rate, selectivity and reaction product yield. Therefore one of the most important task of biochemistry is determination of mechanism of enzyme activity. However enzyme-catalysed reactions are multi-stage and multi-component reactions. As a result previous elaborated simplification methods usually allow to describe investigated reaction qualitatively only. Quantitative results can be obtain owing to calculation methods without simplifications taking into account nonlinear nature of studied process.

ATP hydrolysis by Mg^{2+}-ATPase situated in the plasma membrane is one of the most important reactions responsible for cell vital function. This process is coupled to the active ion transport which is necessary for ion gradients maintenance.

It is determined that this reaction proceeds in presence of three components – magnesium, ATP and Mg^{2+}-ATPase and if one of them is absent in mixture then the reaction can not start. Thus we can conclude that the reaction of ATP hydrolysis passes through ternary enzyme-substrate complex formation (enzyme-Mg^{2+}-ATP). However detailed mechanism of this reaction is unclear up to now. Therefore we were assumed that in initial time each of three starting substances (Mg^{2+}, ATP and enzyme) could combine into complexes in couples with another participants of this process. Stability of this complexes depends on value of its equilibrium constants. Then the third component can associate with present complexes producing triple enzyme-substrat complex (enzyme- Mg^{2+}- ATP). The last complex dissociates to product, enzyme and magnesium cation. Such approach allows to take into account all possible interactions in the chosen system and then to investigate overall process in detail avoiding simplifications during calculations.

For theoretical investigation of ATP hydrolysis process we elaborate the nonlinear dynamic model of kinetics of enzyme-catalysed reaction. It is a system of eight differential equations which take into account behavior in the time of concentrations of each of eight participants of reaction. This system of equations has been solved by numerical method and concentrations of all reaction participants as a function of the time have been calculated. All three possible pathways of the ATP hydrolysis process have been examined separately and as a whole. Calculations of the reaction rate as a function of the concentrations both magnesium and ATP have been carried out in the concentration range similar to experimental conditions.

It is discovered that involving in reaction added pathways provoke appearance of the qualitative new result which is not observed neither “main” nor ‘added” pathway separately. It is a fundamental distinction from the Michaelis-Menten model where added of additional stages has not an influence on shape of the dependence of initial rate on substrate concentration. It is shown that if ATP hydrolysis reaction proceeds via more than one pathway then maximum appears on the plots of initial reaction rate on initial concentration ATP or magnesium. Position of the maximum corresponds with concentration of the component which concentration is fixed. However this position can move in one or another direction on 1-2 order of magnitude depending on ratio of rate constants of all stages. Mechanism of the maximum formation has been established. Thus shape of the plots of initial rate *vs* concentrations magnesium and ATP allows to determine probable mechanism of reaction (related to the possible pathways of reaction proceeding).

Obtained results allow to explain some experimental data of hydrolysis ATP and active ion transport. Represented kinetic scheme also may be applied to another enzyme-catalysed reactions where the metal ions or another substances which can form complexes with other participants of the enzyme-catalysed reaction take part in the reaction together with substrate. Therefore the results obtained in our investigation may be relate to such reactions in full measure.

Symmetry and charge stoichiometry of the cubic nanoparticles of metal monoxides with rocksalt-type structure

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Theoretical simulation of the bulk and surface properties of solids with high-coordinated atoms meets some difficulties connected with the choice of appropriate models capable to describe simultaneously high symmetry of the nanocluster (which is a characteristic of local atomic environment) and its charge stoichiometry. The attempts to build an atom-centered model often result in violation of the accordance in the numbers of metal and non-metal atoms.

In case of magnesium oxide and its structural analogues, two types of cubic cluster models were used. The first one, for example Mg-centered $Mg_{14}O_{13}$ or O-centered $Mg_{13}O_{14}$, is characterized by an excess of metal or non-metal atoms and so leads to a wrong description of the properties controlled by the electron distribution over frontier orbitals [1]. The second one consists in addition or removing some electrons, so that the cluster bears an excessive negative ($Mg_{13}O_{14}^{2-}$) or positive ($Mg_{14}O_{13}^{2+}$) electric charge that causes a considerable shift of the energy levels of the frontier orbitals [2]. Meanwhile it is well known that solid oxide particles can easily interact with water vapors so their surface layers convert into respective hydroxides due to dissociation of water molecules:

$$MeO + H_2O \rightarrow Me(OH)_2.$$

So one can suggest that every metal atom within the surface layer of an oxide nanopatricle should be bound with at least one hydroxyl group whereas every oxygen atom has to be bound with hydrogen one so forming a high coordinated surface hydroxyl group.

It is easily can be seen that all atom-centered cubic monoxide clusters can be divided into two classes, depending on the number (k) of atoms at the edge. If it is $k=4n+1$, the type of central atom coincides with that of the atoms in the centers of faces and in the apexes, and there is an excess of such atoms in the cluster. Alternatively, if it is $k=4n-1$, the types of central atom and of those in the centers of faces are different, and there is a lack of atoms such as that stationed in the center.

Let us count the number of hydroxyl groups and hydrogen atoms necessary to cover nanoparticle surface. First of all, in the case of metal-centered cluster with $k=4n+1$, the number of hydroxyl groups is as follows: 8 at the apexes, $12\cdot(2n-1)$ at the edges, $6\cdot(8n^2-4n+1)$ at the faces, totally $48n^2+2$, whereas number of hydrogen atoms is $12\cdot(2n)$ at the edges and $6\cdot(8n^2-4n)$ at the faces, totally $48n^2$. Thus, two excess positive electron charges are compensated with two excess hydroxide ions. In case of oxygen-centered cluster, these quantities should be exchanged. Analogously, in the case of metal-centered cluster with $k=4n-1$, the number of hydroxyl groups is as follows: $12\cdot(2n-1)$ at the edges and $6\cdot(8n^2-12n+4)$ at the faces, totally $48n^2-48n+12$, whereas the number of hydrogen atoms is 8 at the apexes, $12\cdot(2n-2)$ at the edges and $6\cdot(8n^2-12n+5)$ at the faces, totally $48n^2-48n+14$. Thus, two excess negative electron charges are compensated with two excess protons, and vice versa, if the cluster is oxygen-centered, two excess positive electron charges are compensated with two excess hydroxide ions.

We carried out quantum chemical calculations within *ab initio* (with 3-21G basis set) and semi-empirical (PM3) approximations of the equilibrium geometries and electronic structure of the MgO (Mg- and O-centered) cubic clusters (k values being equal to 3 and 5) with totally hydroxylated surfaces. The results obtained are in a good agreement with experimental data.

1. V.A. Lobach, I.R. Rubin, *Phys. Stat. Sol. (b)*, 160, N 2 (1990) 505.
2. E.P. Mikheeva, S.F. Ruzankin, G.M. Zhidomirov, *Rus. J. Struct. Chem.*, 36, N 1 (1995) 16.

A quantum chemical study on the relative stabilities and red-ox properties of individual and silica supported molybdenum oxo-species

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Supported molybdena systems are widely used in a number of industrially important catalytic processes (selective oxidation, hydrodesulfurisation, metathesis). Therefore, much efforts are being made to the synthesis of the model supported molybdena systems and experimental characterisation of catalytic surface species [1, 2]. The interaction of the molybdenum precursor with the support surface and Red-Ox transformations of surface molybdenum oxo-species play an important role in the catalysts synthesis and activation. Quantum chemical simulation is a consistent way to examine surface properties of catalytic systems at atomic level.

The undertaken research was aimed at an ab initio examination of the cluster models simulated for bulk molybdenum trioxide and for silica supported molybdenum oxo-species. All calculations were carried out within the framework of non-empirical Hartree-Fock SCF MO LCAO approximation by the use of the GAMESS program and the Stevens-Basch-Krauss-Jasien-Cundari valence basis set.

We calculated the geometry and total energies of a number of molecular models which simulated bulk molybdena in which all Mo atoms are six-coordinated. The total energies calculated for such structures were used for theoretical estimation of the cohesion energy. In parallel, we considered two types of the reactions resulting in the formation of surface species due to molybdena-silica interaction. The first route is association:

$$MoO_3 + Si(OH)_4 \rightarrow O_3Mo...O(H)\text{-}Si(OH)_3$$

whereas the alternative one is condensation:

$$HO\text{-}MoO_2\text{-}OH + HO\text{-}Si(OH)_3 \rightarrow HO\text{-}MoO_2\text{-}O\text{-}Si(OH)_3 + H_2O.$$

The tetrahedral molybdenum atom in surface species can interact with two water molecules. Moreover, our calculations have testified that on the surface of silica support the six-coordinated molybdenum oxo-species are more stable in comparison with their four-coordinated counterparts.

Molybdenum(VI) oxo-species can easily be reduced with the formation of molybdenum(V). We decided to use the calculated electron affinities (EA) as a criteria for the prediction of the behaviour of molybdenum(VI) oxo-species in Red-Ox processes. The reducibility of isomeric molybdenum oxo- and hydroxo-species, for example $(HO)_4MoO$ and $H_2MoO_4{\cdot}H_2O$, correlate with their relative total energies: the more stable isomer has relatively smaller value of the EA. The increase of Mo coordination numbers due to hydration leads to decrease of the EA. The molybdenum oxo-species anchored to silica matrix have the EAs that considerably depend on the strain of the structures: the lesser strain, the lesser the EA. Thus, a row of reducibility appears to be the following:

$$MoO_3(gas) > (HO)_4Si_2MoO_5 > (HO)_6Si_3MoO_6 > H_2Mo_2O_7 > MoO_3(bulk) > H_2MoO_4.$$

1. A.A. Gomenyuk, I.V. Babich, Yu.V. Plyuto, and A.A. Chuiko, *Rus. J. Phys. Chem.* 74 (2000) 799.
2. Yu. V. Plyuto, I.V. Babich, I.V. Plyuto, A.D. Van Langeveld, and J.A. Moulin, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 125 (1997) 225.

The mathematical model of the gene network controlling terminal CD4$^+$-lymphocytes differentiation

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We suggested a cluster idea of the gene network structure to provide a framework for the analysis of cell differentiation. In our opinion, cell differentiation is a result of exact coordinated activity of cellular genes united by intracellular signal transduction cascades into gene network. Separate module of this network is the genes cluster – group of together expressed genes, which are specific only for certain stage of cell differentiation and execute program of this stage. Individual genes cluster is constituted by genes of four classes: a) gene-activator; its protein (transcription factor) supports activity of the own gene (positive feedback) as well as all other genes of this cluster and determines thus their belonging to this exactly but not other genes cluster; b) genes-differentiators; their proteins execute individual stage of cell differentiation; c) genes-suppressors, which suppress activity of genes clusters responsible for other possible directions of cell differentiation; d) genes-repressors, which inactivate clusters that completed realization of differentiation stages corresponding to their [1]. The choice of direction of the next differentiation stage takes place after the completion of each previous differentiation stage. Cell receptor, joining specific to its cytokine, activates the expression of gene-activator, which belonged to one among clusters of subsequent differentiation stage. As a result, genes cluster, launched in that way, realizes the following specialization stage and so on [1,2].

This idea accords with lymphocytes development mechanisms discovered today. In particular, T-bet and GATA-3 proteins are transcription factors, which support own genes activity, coordinate expression of some other lymphoid-specific genes and thus control Th1- and Th2-specialization of CD4$^+$-lymphocytes. Received from microenvironmental cells, signal (γ-interferon or IL-4) is recognized by transmembrane receptors that activate corresponding transcription factor gene (T-bet or GATA-3, respectively) through specific signal transduction-activated transcription factor (STAT1 or STAT6). T-bet and GATA-3 genes expression is alternative and is autoactivated by intacellular and extracellular positive feedbacks [3]. Therefore this system works as a bistable switch that enables the triggering of a differentiation program by transient extracellular inductive signals. There are several means for the regulation of T-bet/GATA-3 ratio (and thus for the decision of developing CD4$^+$-cell fate), including direct inhibition of transcription factor activity, its sequestration by a binding protein, repression of basal transcription or breakup of autoactivation feedback. To investigate the influence of all these factors on final result, mathematical analysis of the system behavior is necessary. All things considered, we develop a mathematical model for the transcriptional regulatory network controlling the terminal stage of CD4$^+$-cell differentiation programs.

The intracellular, but not extracellular, autoactivation feedback in transcription factor gene expression plays the crucial role for robustness and irreversibility of the cell differentiation.

1. Halytskiy V.A. *Cell determination and differentiation: a concept of gene clusters*. Cytology, 2001; 43(10): 913-925 (in Russian).
2. Halytskiy V.A. *Gene networks of cell differentiation and phenomenon of tumour growth.* Ukrainian Biochem. J., 2005; 77(2, sp. iss.): 111.
3. Hatton R.D., Weaver C.D. *T-bet or not T-bet*. Science, 2003; 302: 993-994.

About influence of the microscopic structure of the surfaces on the interaction potential in the vacuum gap between two metals with the ordered submonolayer of the adsorbed coatings

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When the distance L between two flat surfaces is small $L \le 3-40\overset{0}{A}$, the metals (semiconductors, dielectrics) cannot consider independently because the image potential $V^0(x)$ forms a potential barrier in a small vacuum interval between two half-limited metals. This barrier is determined by the difference in the electronic structure of the two metals. The correct accounting of the electronic structure in the metals provides finiteness and continuity of the summarized potential $V(\vec{r})$ at the interfaces, which essentially differs from classical received within the framework of a local (classical) electrostatics [1]. This theory is correct for the quasi-neutral clean metal surfaces, when the summarized charge density σ_1 and σ_2 on the metal/vacuum interfaces is zero. However in a number of cases, for example as a result of the adsorption on the surfaces, the electroneutrality condition is disturbed.

In present paper the structure component $\Delta V_{st}(\vec{r})$ of the interaction potential in the small vacuum interval between two flat metals with the ordered submonolayer of the adsorbed coatings, which is determined by the microscopic (atomic) structure of the surfaces, is calculated theoretically in the framework of a non-local electrostatics.

In this work we take into account the charge state of the metal surfaces, when $\sigma_1, \sigma_2 \ne 0$. The distribution of the common potential barrier $V(x)$ formed between two closely spaced metals with the ordered lattice of the adsorbed atoms on the both metal surfaces is calculated, using the Green's functions of the nonlocal Poisson equation [2]. For the simplification of the calculations and for the best presentation we considered the identical metals with the different charge densities $\sigma_1 \ne \sigma_2$ on the metal facets. The dielectric functions $\varepsilon_{1,2}(\vec{k})$ of the similar metals we determine in the Thomas-Fermi approximation (TFA). The distribution of the charge component $\Delta V(\vec{r})$ and the common potential $V(\vec{r})$ in the vacuum gap with the account of the microscopic structure of the fixed adsorbed lattices at the metal surfaces is determined.

It is shown that the contribution of the microscopic structure of the charged surfaces increases with the decreasing of the separated distance L and with the increasing of the value of the charge on the adatoms. The accounting of the structure component $\Delta V_{st}(\vec{r})$ determines the lateral change of the potential barrier height in the vacuum gap and can lead to the local increasing (decreasing) of the full potential in the vacuum interval.

It is shown that the local lateral lowering of the potential barrier height along the interfaces can result to the appearance the well-ordered lattice of the structured potential $\Delta V_{st}(\vec{r})$ inside the small vacuum gap with the lattice parameter, which exceeds the parameters of the ordered adsorbed lattices for the both metal surfaces.

1. J.G.Simmons J.Appl.Phys., **35,** 2472 (1964).
2. L.G.Il'chenko, T.V.Goraychuk, Surf. Sci. **478,** 169 (2001).

Quantum-chemical study of structural rigidity of the β-(1,3)- and β-(1,6)-glucan dimers

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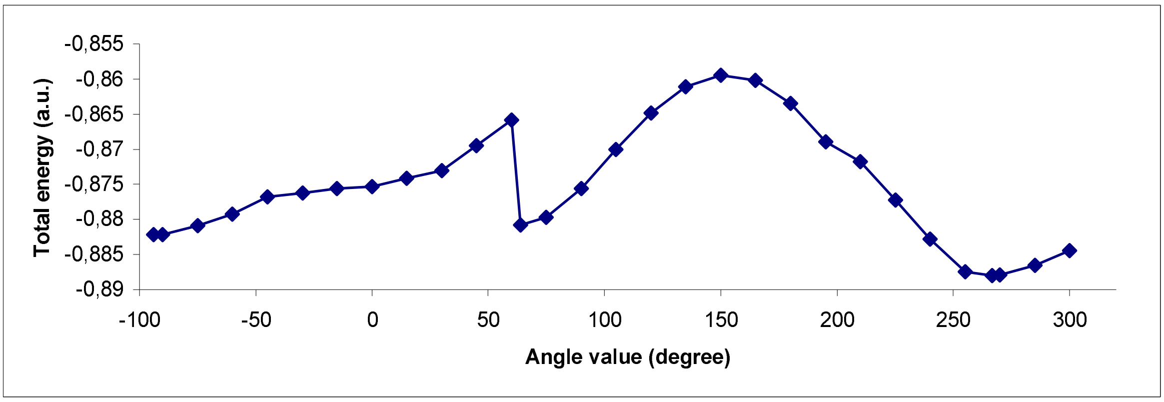
The β-(1,3)- and β-(1,6)-glucans - linear biopolymer compounds of the D-glucose which are bound by means of glycoside bonds – greatly signify in composition of fungi cell wall. Study of structural rigidity of the oligosaccharide polymer chain and energy of glycoside bonds hydrolysis is one of the important problems. For low-polymeric fraction it is especially important to know about rotation possibility of separate elements of the polymer chain (glucopyranose rings) about the glycoside bonds. The probability of this process can be estimated, for example, by definition of energy value requisite to overcome the rotation potential barrier at transition from one conformer to another. The potential barrier magnitude can answer, in particular, the problems about the rigidity (lability) of separate polymer rings and energy of the glycoside bonds hydrolysis.

The computations have been carried out by the methods of density functional diffusion (DFT methods) widely used recently for many biological problems solution. We have applied the most popular B3LYP potential including the wide basis sets in calculating scheme. The GAUSSIAN 98 (ver.A11.2) quantum-chemical program was used. All calculations were spent with regard for complete or partial (when one of the torsion (dihedral) angles was fixed) optimization of geometrical position of each atom in system under discussion.

The total energy of the D-glucopyranose dimer (which is the elementary model of the β-(1,3)-glucan) depending on the torsion angle value corresponding to rotation about the glycoside bond is shown on the figure below. The torsion angle varied with a step in 15 degrees from -90 up to 270 degrees that corresponds to complete rotation about the bond. In points of local minimum the geometry refinement was spent by complete optimization. Complicated curve with a lot of local minimums (stable geometric structures) and maxima that correspond to transient states between various local minimums are pointed out on the graph. In this case we studied local minimums only, because the searching of a global minimum was not included into an orb of our interests and there is no ration to structure of the dimer investigated. The dissociation energy of the β-(1,3)-glycoside bond determined from the graph is equal 6.05 kkal / mol.



The computations of β-(1,6)-glucan dimer have been carried out similarly. In this case the torsion angle varied with a step in 15 degrees from 90 up to 450 degrees (complete rotation about the bond). The determined dissociation energy of the β-(1,3)-glycoside bond is equal 1.87 kkal / mol.

Thus, the spent calculations testify that β-(1,3)-glycoside bond is more stable to dissociation in neutral medium.

The study of the organic compounds electronic structure by the natural bond orbital method. 1. Interactions of OY and SY groups (Y = H, CH_3, CF_3) with aromatic, double and triple bond unsaturated moieties

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The compounds possessing general formula C_6H_5XY, *p*-$RC_6H_4XCH_3$, $H_2C{=}CHXY$, *trans*-$RCH{=}CHXCH_3$ and $HC{\equiv}CXY$, where: X = O or S, Y = H, CH_3 or CF_3, *p*-R = NH_2, OCH_3, CH_3, F, Cl, CN, NO_2, *trans*-R = NH_2 or NO_2 were studied at *MP2(full)/6-31G** and *MP2(full)/6-31+G** levels of the theory. Analysis of PES was performed; nature of stationary points was verified by analysis the matrices of the energy second derivatives, the values of the rotational barrier of internal rotation about the C_{sp^2}–X were estimated. Enlarging of steric hindrance of the Y group (H < CH_3 < CF_3) in compounds C_6H_5XY with the same X leads to decreasing of percentage of the planer forms with $\varphi = 0°$ and 180° and percentage of the orthogonal form is increasing correspondingly. For the compounds $H_2C{=}CHXY$ percentage of the s-*cis*-comformer with $\varphi = 0°$ is decreasing and percentage of the s-*trans*-conformer with $\varphi = 180°$ is increasing. The planar conformations are more stable with the same Y group for the both aromatic and vinyl ethers then sulfides. Electronodonor substituents for the *p*-$RC_6H_4XCH_3$ and *trans*-$RCH{=}CHXCH_3$ compounds cause decreasing stability of the planar conformations. Electronoacceptor substituents increase stability of the planar forms. Two LEPs of O and S atoms are different according NBO formalism. The hybrid natural orbital of one LEP (n_σ) has approximately 66 - 68 % s-character for S atom and 36 – 45 % for O atom. While the other LEP (n_π) is practically "pure" *p*-orbital for both atoms O and S. The hybrid LEP has less energy of donor-acceptor interactions with antibonding orbitals of the unsaturated moieties then LEP (n_π). The energy of n_π,π^*-interactions is maximal for the planar conformations. The interactions are energetically preferable for s-*cis*-comformations of the $H_2C{=}CHXY$ compounds rather then for the s-*trans*-conformations and for O atom containing molecules rather then the sulfides. The energy of interactions is decreasing in a row CH_3 > H > CF_3 for the Y groups. Electronoacceptor *p*-R and *trans*-R substituents increase energy of the n_π,π^*- interactions and electronodonor *p*-R and *trans*-R substituents decrease the energy. The energy of the n_π,π^*- interactions for the compounds with the same X atom and conformation is decreasing in a row: triple bond > double bond > aromatic ring. Analysis of energies, populations and dipole moments of natural bond orbitals of the compounds under study shows that leading causes of the unsaturated moieties polarity are electronegativity of the X atoms and conformational behavior. Donor-acceptor interactions play secondary role and depends on molecular conformations. NBO analysis of wave functions gives quantitive picture of interactions of O and S atoms with aromatic ring, double and triple bonds.

Interaction of Organic and Carboxylic acids, and Proteins with Silica surface in Aqueous Medium

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This study focused on interaction of amino acids, peptides, and proteins with nanosilica surface in aqueous media was carried out using quantum chemical methods such as DFT and HF with consideration for the effect of solvents. Gibbs free energy of solvation, structural and electronic parameters of silica clusters, and adsorption complexes with biomolecules were calculated using solvation models SM5.42/HF/6-31G(d), SM5.42/HF/PM3, SM5.42R/HF/6-31G(d), and SM5.42R/B3LYP/6-31G(d) by means of the GAMESOL (version 3.1 modified by addition of the DFT method [1]) . Geometry relaxation in liquid phase was taken into account using the SM5.42 method.

It has been shown that the nature of an adsorbate, an adsorbent, and a solvent as well as the nanosilica structure affects the adsorption of biomolecules. The adsorption of low molecular polar molecules onto the nanosilica surface is not thermodynamically favorable from highly polar media. Several factors that promote the adsorption of biomolecules to the surface of nanosilica from the liquid media have been identified. It has been obtained that a structure of side groups of amino acids has a large effect on their adsorption interactions with the silica surface in the aqueous medium. Hydrophobic effect plays a significant role in the case of the adsorption of amino acids with nonpolar side groups. An increase in the accessible surface of the nonpolar side groups in a sequence Gly → Ala → Val → Leu leads to increase in the Gibbs free energy of hydration and reduction in the Gibbs free energy of adsorption. It has been confirmed that, as opposed to hydrophobic nanosilica surface modified by trimethylsilyl groups, the hydrophilic nanosilica surface allows preservation of the conformation of proteins. In contrast, the hydrophobic nanosilica surface induces irreversible changes to the geometry of proteins on the adsorption. It has been shown that amino acid molecules in the aqueous media promote the hydrolysis of the siloxane bonds in the silica surface layer leading to dissolution of a portion of silica. The formation of a complex $\equiv Si(OH) \leftarrow OH^-$, wich can be considered as an initial stage of silica surface decomposition, with simultaneous proton attachment to uncharged amino group of Gly ($\equiv Si(OH) + NH_2CH_2COOH + H_2O \rightarrow \equiv Si(OH) \leftarrow OH^- + NH_3^+ CH_2COOH$) results in change in the Gibbs free energy of solvation $\Delta G_s = -20$ kJ/mol (SM5.42R/B3LYP/6-31G(d).

When the solvation effects are taken into account, calculations of the Gibbs free energy of the adsorption provide a valuable tool to predict adsorption interactions of biomolecules with nanosilica and allow predicting the conformational and tautomeric changes of biomolecules in the adsorbed state. For example, on the base of experimental (adsorptional and spectroscopy) and calculated (Gibbs free energy) results the adsorption of cinnamic acids on the silica surface has been studied from a water-ethanol solution. It was experimentally and theoretically obtained that cinnamic acid derivatives are immobilized on the silica surface by the hydrogen bonding between phenol's hydroxyl groups of acids dimers with silanol groups of silica.

1. (a) Xidos, J. D., Li, J., Zhu, T., Hawkins, G. D., Thompson, J. D., Chuang, Y.-Y., Fast, P. L., Liotard, D. A., Rinaldi, D., Cramer, C. J., and Truhlar, D. G., GAMESOL–version 3.1, University of Minnesota, Minneapolis, 2002, based on the General Atomic and Molecular Electronic Structure System (GAMESS) as described in Schmidt, M. W., Baldridge, K. K., Boatz, J. A., Elbert, S. T., Gordon, M. S., Jensen, J. H., Koseki, S., Matsunaga, N., Nguyen, K. A., Su, S. J., Windus, T. L., Dupuis, M., and Montgomery, J.A., *J. Comp. Chem.* 14, 1347 (1993). (b) Cramer, C.J., and Truhlar, D.G., *Chem Rev.* 99, 2161 (1999).

PC-oriented program complex for the simulation of large system, model verification and the evaluation of some macroscopic properties

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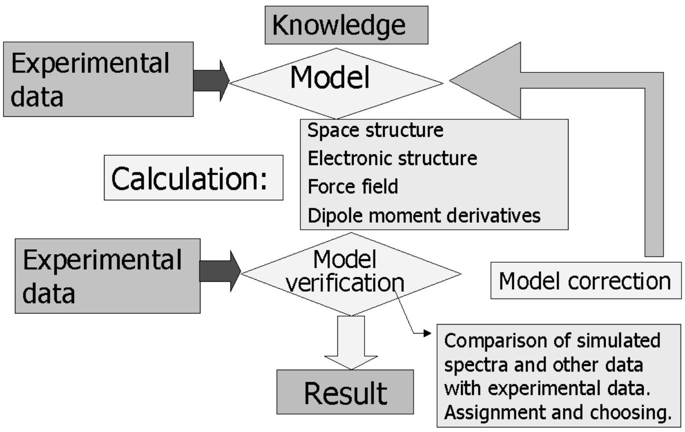
In order to investigate broad classes of practically important materials, systems and processes a PC-oriented program complexes "QuChem" and COSPECO for model system simulation and verification as well as evaluation of some macroscopic properties have been developed and are supported. The quantum chemical base of these programs is well-known semiempirical methods AM1 and PM3 and, recently developed methods MSINDO and MSNDDO, applicable for transition metals [1-3]. The last two methods' codes were obtained directly from developers and have been incorporated into our programs. The MSINDO and MSNDDO methods have shown the best results for the transition metal compound simulation among semiempirical methods.

The basic fundamentals for the "QuChem" and COSPECO program data treatment were described [4], too. Below we would like to show main cycle for model developing, computing and verification. Our main method for verification is computational vibrational spectroscopy, including inelastic neutron scattering, infrared and Raman spectroscopy.

'Technology following' methodology



We call this used methodology as "Technology following" [5-6], because not only the molecules or clusters, but the main features of technological processes are simulated. Some results concerning small silica particles and different silica materials production [7], will be presented and accompanied with computer animation. Recent results about structure and properties of amorphous carbon and carbon-based materials, including magnetic properties of some carbons, will be presented, too.

1. D.N. Nanda, K. Jug, Theoret. Chim. Acta, v. 57, 95 (1980)
2. B. Ahlswede, K. Jug, J. Comput. Chem. v. 20, 563 (1999); ibid. 572
3. T. Bredow, G. Geudtner, K. Jug, J. Comput. Chem. v. 22, 861 (2001)
4. V.Khavryutchenko. Eurasian ChemTech Journal, v. 6, 157 (2004)
5. V.D. Khavryutchenko, A.V. Khavryutchenko, H. Barthel, B. Poumellec, J.-O. Roszinski. Int. Conf.-on Silica Science and Technology. Extended abstracts Mulhouse, France, Sept. 3-6, 2001, p. 14
6. A.V.Khavryutchenko, V.D.Khavryutchenko. Zeitschrift für Naturforschung A, v. 60a, No 1/2 (2005), pp. 41–47.
7. V Khavryutchenko, J Garapon, B Poumellec. Modelling Simul. Mater. Sci. Eng. v. 9, pp. 465-483, (2001)

Conformational Analysis of CL-20. DFT study

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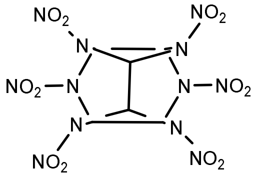
The 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20, 1) was recently developed for different military and industrial purposes.

The basic structure of CL-20 consists of a rigid isowurtzitane cage, which includes two five-member rings (FMRs) and a six-member ring (SMR). Two FMRs link each other by the C-C bond at the top and project outwards at two pairs of N atoms. There is considerable tension in the skeleton of CL-20. The C-C bond linking the two FMRs and the six bonds of SMR are important stabilization factors. The SMR is boat-shape with the prows directed downwards. The CL20 molecule has six nitro groups attached to each of the six bridging nitrogen atoms in the cage. The spatial orientation of the nitro group has little influence on the skeleton. The N-N bonds of CL-20 are more fragile than the other bonds of the considered compound.



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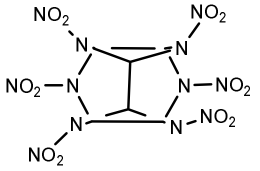

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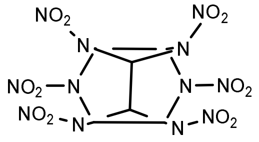

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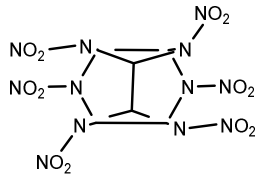

1d

All spatial orientations of these nitro groups with respect to the FMRs and SMR in the cage, the differences in crystal lattice packing, and the number of molecules per unit cell define several possible polymorphs. So far, five polymorphs, a-, b-, g-, e- and z-CL-20, were isolated experimentally. The relationships between the conformations and the molecular properties of CL-20 have been detail analyzed by Zhou et al.[1] in a previous work using the B3LYP/6-31G(d,p) level of theory. The authors have investigated the conformational properties of CL-20 and have shown, that among four possible conformers (1a – 1d), conformer 1d is the most stable.

In present work conformational analysis of CL-20 molecule have been performing using quantum-chemical methods. DFT calculations were performed with the program GAUSSIAN98. The fully optimized geometries of conformers **1a-1d** have been calculated with at the B3LYP/6-31G(d) level of theory. In addition, calculations have been done with the expanded 6-311++G(d,p) (using the B3LYP functional) set. The minima of the potential surface were found by relaxing the geometric parameters with standard optimization methods. Analytical force constants were derived using all investigated theoretical levels. Obtained data have been compared to experimental FTIR spectrum of CL-20 molecule.[2]

1. Zhou, G.; Wang, J.; He, W.-D.; Wong, N.-B.; Tian, A.; Li, W.-K. Journal of Molecular Structure (Theochem) 2002, 589–590, 273.
2. P. Honea, M. Qasim, H. Fredrickson, J. Furey, S. Okovytyy, Y. Kholod, J. Leszczynski. // Extended Abstracts of Conference on Current Trends in Computational Chemistry – Jackson, MS – 2004 – P. 71.

The polyoxygen molecular mechanism of alkenes oxidation. *Ab initio* quantum-chemical study

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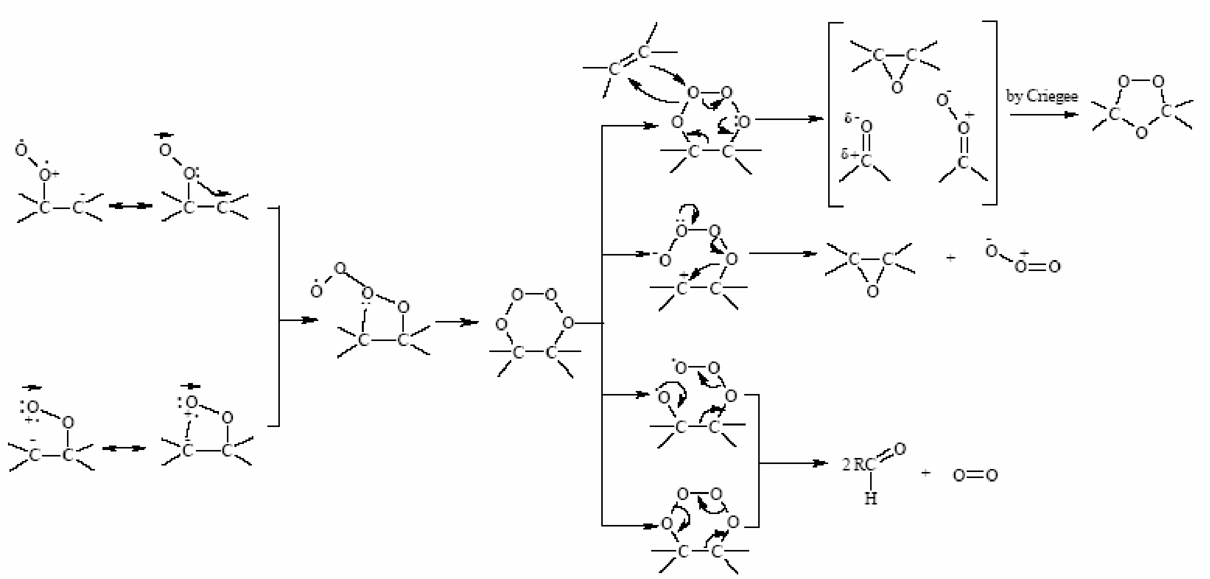
The oxidation appears to be the essence of numerous chemical and biochemical processes caused by the action of bonded or molecular oxygen. Synthesis of epoxides through interaction between olefins and molecular oxygen is of wide use in industry. Although a number of experimental and theoretical studies of this process exist, its mechanism is still controversial.

In the present work a quantum-chemical investigation of the potential energy surface (PES) of ethylene oxidation with molecular oxygen through a polyoxygen intermediate has been carried out. Geometry optimization of all energy minima and transition states structures has been performed at the B3LYP/6-31G(d), BHandHLYP/6-31G(d), and CASSCF(8,8)/6-31G(d) level of theory using the GAUSSIAN03 program. An influence of a solvent has been considered using the macroscopic PCM approach. Singlet and triplet stability of Hartry-Fock solution has been checked for all critical points.



Two minima corresponded to dioxethane type and oxirane type complexes have been located at the PES of interaction of ethylene with triplet oxygen. The first isomer is energetically more preferable compared with the second type isomer due to larger distortion of the interacted orbitals. Addition of the second oxygen molecule to the dioxethane type complex results in the 1,2,3,4-tetraoxane. Attack of the formed intermediate with an alkene, or C-O bond polarization leads to different heterolytic transformations, which involve energetically preferable synchronous transfer of the electronic pairs. Alkene attack results in transfer of an oxygen atom to an alkene to form an epoxide and the Criegee intermediate. Orientation of orbitals in the 1,2,3,4-tetraoxane of C-O bond haterolysis creates a possibility for the epoxy ring closure with throw out of the ozone molecule. 1,2,3,4-tetraoxane can degrade forming an oxygen molecule and two aldehyde molecules.

ISMOL – a hybrid type database on the molecular spectral constants

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Automatization of the physical chemistry research based on the vibrational spectroscopy experiment adds special significance to the problems of the correct experimental data processing and interpretation. This could be greatly facilitated by extensive and well-developed databases on the molecular constants. A modern vision of the electronic reference tools assumes that such a tool might (and should) include not just an information database (experimental and calculated data, information on the used models, other reference data) but rather be integrated with a certain software package allowing to immediately obtain various theoretical estimates. This kind of reference database is referred to as hybrid. Below we suggest a set of requirements that a modern database on the spectral constants for the polyatomic molecules should satisfy; we think this set of requirements is necessary for creating a tool useful and efficient in applied as well as fundamental research.

- The database scope should be limited as regards the variety of the compound classes and/or some other auxiliary criteria.
- It should contain an extensive set of reference IR absorption spectra recorded under conditions close to the normal conditions of the existence of each substance, and with sufficient resolution.
- It should contain a database on the force constants and structural parameters of the molecules for fast evaluation of theoretical vibrational spectra of the molecules and their thermodynamic functions.
- It should be integrated with software package allowing solution of direct and inverse spectroscopic problems on the base of stable numerical methods. Software package should allow the user to choose appropriate set of molecular coordinates and force field model, and obtain a collection of force constants transferable in the series of similar molecules. Such constants, once calculated, may be added to the database.
- It should include the results of quantum chemistry calculations corresponding to a certain theory level (or maybe a series of these levels within the framework of the so-called “model chemistry”); these results should ensure reliable prediction of the properties of the substances from the database scope;
- It should provide the possibility of identifying components in a mixture of substances and solving some other problems of molecular spectra interpretation.

The requirements listed above were used as guidelines for designing ISMOL database on the spectral characteristics of the compounds found in the crude oil and refinement products that was created by the authors in the Moscow State University (M.V.Lomonosov). This reference tool is based on the original program environment allowing storage, management and processing spectral data, with the opportunities of preparing output information in the text, graphic and tabular form. Software development was done in the Microsoft Developer Studio environment with the help of Microsoft Visual C++ compiler and the use of MFC (Microsoft Foundation Classes) technology.

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Quantum-chemical study of active carbon

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Active carbons (AC) are widely used in processes of reduction and oxidizing sorption, in scientific researches and industry for separation, concentration and deep purification of substances, at creation of anode paste for chemical current sources, for problem-solving of environmental preservation and as catalysts and supporting medium. AC's high anisotropy is determined by various structural defects of graphen planes, by presence of heteroatoms (B, N, O) in surface functional groups or replacing carbon atoms in the carbon matrix.

The mechanism of influence of heteroatoms (B, N, O) on physical-chemical, electrochemical, adsorption and catalytic properties of carbon matrix as well as mechanism of sorption selectivity of AC in relation to electropositive metals is not conclusively established and the results available are inconsistent. Moreover, the influence of oxygen on kinetics of electrochemical potential formation and the mechanism of sorption of Cu, Ag, Au are not investigated till now. The electron transfer from the AC matrix to the oxygen molecule or to ion of metal is characteristic feature for such processes. It is determined by work function of electron from the carbon matrix (electron-donor ability, Fermi level), that is depends on the electron-power characteristics of AC. The analysis of ESCA C (1s) spectra of SKN carbons testifies that the atoms of carbon are in sp^2- hybridized state mainly (C1s=284,8 eV; 65÷ 85 %). It allows to use the model graphite-like clusters $C_{96-n}X_n$ ($X > B, N, O$) containing 37 hexagonal cells in performing the quantum-chemical calculations.

The systematical research of influence of degree of SKN carbon oxidation (SEC) on kinetics of stationary potential formation and sorption of copper subgroup metals including AM1 calculations of the electronic structure of model clusters (geometrical structure, charge distributions and energies of boundary molecular orbitals, E_{HOMO} and E_{LUMO}) with various amount of heteroatoms in a carbon matrix and in surface functional groups were carried out.

It was established that:

- Progressing carbon oxidation (the accumulation of the total amount and different oxygen forms) gives a considerable change its electron-donor properties. The mechanism of stationary potential formation for weak-oxidizing carbon (SEC=0,2 ÷1,0 mg-eqv/g) is determined by electron density transfer from the carbon matrix to the oxygen molecule and it is under control of SKN semi-conductor properties (Fermi level, ionization potential, E_{HOMO} value), and for strong-oxidizing carbon (SEC>1,0 mg-eqv/g) it is determined by change of geometrical structure of the surface of carbon matrix. The method of estimation of electron-donor abilities of carbon materials in aerated electrolytes solutions is offered.
- The mechanism of Au, Ag, Cu reduction is effected by transfer of π-electron density of carbon on 4s, $4p_x$, $4p_y$, $4p_z$ and $3d_{xy}$ atomic orbitals of metal cation (Me^+). The interaction of weak-oxidizing carbon (SEC<1,0 mg-eqv/g) is carried out by the electrochemical mechanism with formation of metal film on the carbon surface, the reduction process occurs in "carbon - Me^+" donor-acceptor complexes is determined by electron-donor abilities of carbon and is orbital-controllable. For strong-oxidizing carbon (SEC>1,0 mg-eqv/g) the amount of oxygen-containing groups (COOH-, mainly) on the carbon surface is increased. The coordination complexes, such as $COO^-…Me+…^-OOC$, can be formed in these systems when the charge-controllable electronic density transfer is carried out from COO^- groups on metal cation.
- The increase of concentration B, N and O heteroatoms in carbon cluster C_{96} is resulted in occurrence of maxima on E_{HOMO}- concentration dependences in 3÷6 % heteroatoms region. It compatibles with change of catalytic activity of nitrogen-containing carbons in reactions of H_2O_2 decomposition and H_2S oxidation, and reduction currents of $Cr_2O_7^{2-}$, O_2 and Fe^{3+} in oxygen-containing carbons. It is shown that the observable effect correlates with change of $p_{\pi\pi}$(C-X) occupation of $C_{96-n}X_n$ clusters, it is caused by influence of heteroatoms on the π-coupling value in the molecular skeleton of cluster.

Molecular structure of β-D-glucosylhydroxymethyluracil: a DFT investigation

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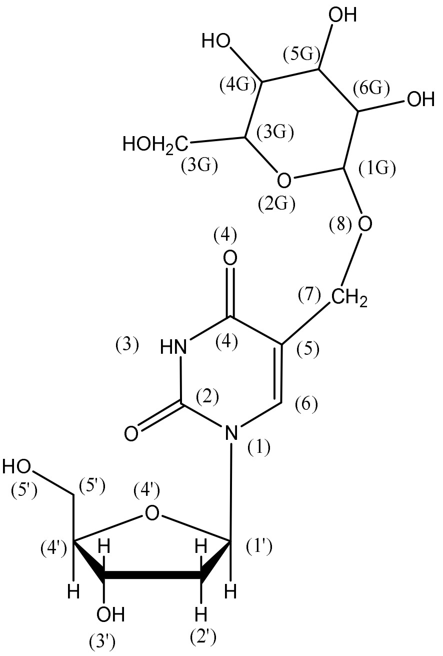

Fig. 1. Structural formula of β-D-glucosylhydroxymethyluracil

A hypermodified nucleoside β-D-glucosylhydroxymethyluracil (Fig.1) was found in DNA of *African trypanosoma brucei* and also present in kinetoplastids of *Leishmania donovani* and *Trypanosoma cruzi*. This hypermodified nucleoside substitutes 0.5-1% of thymine in the DNA [1] and preferentuialy localized in (GGGTTA)n telomere repeats of the DNA. The presence of β-D-glucosylhydroxymethyluracil is correlated with the silencing of telomeric genes [1].

The molecular structure and relative stability of conformers of the hypermodified nucleoside has been obtained and analyzed at the DFT/B3LYP level using the 6-31++G(d, p) basis set. Bader's Atoms in Molecules (AIM) theory has been applied for analysis of the intramolecular hydrogen bonds in the nucleoside.

We have considered four major conformers of the nucleoside, i.e. *north/anti, north/syn, south/anti,* and *south/syn*. The multiple intramolecular hydrogen bonds have been found in all considered conformers. The *syn* conformations of the nucleoside are stabilized by H-bonds of C-H···O type with O(2) acceptor atom. The *anti* conformations in addition to C-H···O hydrogen bonds with O(5') and O(2) acceptor atoms are stabilized also by O(5')-H···O(6G) hydrogen bond between glucose ring and 2'-deoxyribose moiety of the nucleoside.

The arrangement of the glucose ring is determined by O(5')-H···O(6G) hydrogen bond in *anti* conformations and C(6)-H···O(6G) hydrogen bond in *syn* conformations of the nucleoside. The relative free energies (T=298K) of considered *anti* conformers are lower than energies of the corresponding *syn* conformers by to 4-6 kcal/mol.

Hydrogen bonds of β-D-glucosylhydroxymethyluracil could influence on the secondary structure of the DNA containing this hypermodified nucleoside.

1. F. Van Leeuwen, M. C. Taylor, A. Mondragon, H. Moreau, W. Gibson, R. Kieft, and P. Borst *Proc. Natl. Acad. Sci.* USA 95, pp. 2366–2371, 1998.

A DFT simulation of silica surface etching with aqueous sodium hydroxide

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Silica is well known to be resistant against dissolution in many solvents except hydrofluoric acid and alkaline media. There are a lot of experimental data concerning these phenomena and they need a theoretical analysis at atomic scale level. This work is devoted to the simulation of the elementary acts of silica surface interaction with alkaline water solutions.

The calculations were performed using the B3LYP hybrid density functional method implemented in the GAMESS program package. The equilibrium geometric parameters and total energy values for $(NaOH)_m(H_2O)_n$ complexes as well as for those interacting with clusters simulated for silica surface were calculated using the 6-311++G** basis set. In addition, some transition states were localized for various reactions.

When interacting with water molecules, NaOH molecule can form cyclic hydrogen bond tight structures where sodium atom coordinates oxygen atoms of water molecules whereas hydroxyl group forms hydrogen bonds via its oxygen atom with hydrogen ones of water molecules. These species can then are rearranged into another ones characterized by the separation of Na^+ and OH^- ions. In case of NaOH oligomers, analogous phenomena occur but the energetic characteristics deviate considerably.

Siloxane oligomers can form associates with gaseous NaOH molecules. These species then transform into alternative states where Na^+ are substituted for protons of acidic type silanol groups:

$$(HO)_3Si\text{-}OH + NaOH \rightarrow (HO)_3SiO^-Na^+ + H_2O.$$

Such processes are promoted by addition of solvating water molecules and sodium ions so obtain hydrate covers. Alternatively, metal ions can substitute protons of water molecules coordinated to silicon atoms:

$$(HO)_4Si\leftarrow OH_2 + NaOH \rightarrow (HO)_4SiO^-Na^+ + H_2O.$$

The process of Si-O-Si linkage cleavage with alkali hydroxides has been examined. Some anhydrous systems are tested as well as those accompanied with definite quantities of water molecules. Such processes can be described merely due to participation of hydroxide ion in the reaction. Nevertheless the presence of cations affects the values of energetic characteristics of the process. The first step of the above mentioned reaction seems to be an addition of a hydroxide ion to a silicon atom followed by the dissociation of siloxane bond:

$$(HO)_3Si\text{-}O\text{-}Si(OH)_3 + OH^- \rightarrow (HO)_3Si(OH)\text{-}O\text{-}Si(OH)_3^- \rightarrow (HO)_3SiO^- + HOSi(OH)_3.$$

When adding a hydroxide ion, the silicon atom of siloxane cluster changes its coordination sphere from a tetrahedron to a pentagonal bipyramid. So the value of activation energy can be estimated within the frameworks of the deformation model. Really, the true value of this quantity obtained via the saddle point procedure appears to be very close to that evaluated from the deformation energy calculation.

An excess of sodium hydroxide can transform silica patterns into sodium silicate ones. We examined two alternative isomeric forms of the corresponding cluster models differing by the type of sodium ion environment: hydrate shells versus ions directly coordinated to siloxane and/or hydroxyl group oxygen atoms as well as to those connected with silicate ions what are the characteristics of natural hydrated alkali metal silicates. The arrangements between these two structures are rather complicated processes but can be examined separately step-by-step.

Conformation analysis of 25, 27-dipropoxy-11, 23-bis[3-(triethoxysilyl)propyl]calix[4]arene-crowns-6 by quantum – chemical methods

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Crown ethers derived from calix[4]arenes are actively investigated in supramolecular chemistry and separation science [1]. These macrobycyclic compounds show binding properties for alkali metal ions. However both the selectivity as a stability of the complexes seems to be highly dependent on the number of oxygen atoms on the ether bridge and on the conformation of the calixarene skeleton [2]. Particularly interest cause the calix[4]arene-crowns-6 in *1,3-alternate* conformation which show remarkable selectivity in the complexation of cesium ion and, for this reason, are promising in the ^{135}Cs removal from radioactive waste [3].

Previously we reported synthesis and investigation of structural properties of 25, 27-dipropoxy-11,23-bis[3-(triethoxysilyl)propyl]calix[4]arene-crown-6 (Fig. 1) [4]. NMR data testify that the triethoxysilyl derivative of calix[4]arene-crown-6 fixed in 1,3-alternate conformation. The aim of the presented work is to study influence of derivatives nature on the conformation behavior and geometry of calix[4]arene-crown-6 molecule and to compare obtained results with NMR data. An optimization of the geometry of 25, 27-dipropoxy-11, 23-bis[3-(triethoxysilyl)propyl]calix[4]arene-crown-6, where the position of phenolic rings containing propoxy groups is changeable relatively the other aromatic rings, was carried out with quantum-chemical semiempirical AM1 and PM3 methods.

The analysis of results showed that the difference in values of total energies ($\Delta H_{formation}$) of the optimized structures is slight. However it was found that a structure where propoxy groups and triethoxysilyl groups are disposed in different sides of a plane passing through methylene groups which bond aromatic rings is the most energetically favorable (Fig. 1).

Therefore, experimental results are in a good agreement with data obtained with quantum–chemical calculations.

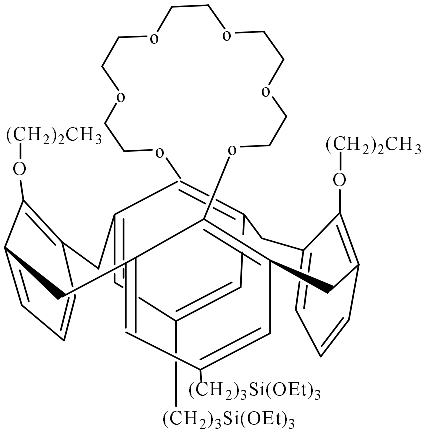

Fig.1

1. Casnati A., Sansone F, Dozol J.-F., J. Incl. Phenom. Macroc. Chem., **41 (**2001) 193.
2. Casnati A., Della Ca N., Sansone F., Ugozzoli F., Ungaro R., Tetrahedron, **60** (2004) 7869.
3. Casnati A., Ungaro R., Asfari Z., and Vicens J., Crown Ethers Derived from Calix[4]arene, in: Z. Asfari, V. Böhmer, J. Harrowfield, and J. Vicens (eds.), Calixarenes 2001, Dordrecht: Kluwer Academic Publishers, 2001, p. 365.
4. Alexeeva E. A., Gren I.A., Kuchma O.V., Zub Yu. L., Chuiko A.A., "25, 27-dipropoxy-11,23-bis[3-(triethoxysilyl)propyl]calix[4]arene-crown-6 – Synthesis and Identification", «Nanosystems, nanomaterials, nanothechnology», 2005 (in press).

The quantum-chemical research of surface elementary processes

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The structure of surface's chemical compounds are defined not only the chemisorption's peculiarities, but the modifying surface transformation too. It does refer not to many layer surface structure formations, but to the chemical and thermal transformations of the new functional groups immobilizing on the surface. The nature of bonding between adsorbat and surface is still subject to some interpretation. Nondissociative adsorption processes are sometimes called molecular adsorption. It is naturally difficult to know how molecules desorbed: molecularly or dissociatively, because it is hard to investigate by experimentally. In such case the quantum-chemical calculation can be very useful instrument for clarification and explanation of the elementary processes on the surfaces during chemisorption.

The quantum-chemical calculations have been provided by the *ab initio* method in the 6-31G basis set to investigate the chemical way to destruct of organic molecules immobilizing on the silica surface. Point defects, stabilized on the activated silica surface have the high reactivity, and they have been used as "foundation" for immobilized on the surface intermediates both diamagnetic and paramagnetic nature. This method is founded effective for obtaining of different chemical structure intermediates. Such structures have high thermal stability and didn't move quickly to be bounded by strong chemical bounds and this fact opens possibility for the study their reactivity and destruction pathways. The subject of research was alkyl-radicals ($CH_3^{\bullet}$, $C_2H_5^{\bullet}$) as one of the representatives of saturated hydrocarbons.

Calculations have been provided both for the isolated molecule and for the immobilizing one on the silica surface. The calculation results have presented in the table.

Destruction way	$E_{destr.\ bind.}$ (a.u.)
$(OH)_3SiO\text{-}CH_2\text{-}CH_2^{\bullet} + H^{\bullet}$	0,1355
$(OH)_3SiO\text{-}CH^{\bullet}\text{-}CH_3 + H^{\bullet}$	0,4845
$(OH)_3SiO^{\bullet} + CH_2^{\bullet}\text{-}CH_3$	0,1026
$(OH)_3SiO\text{-}CH_2^{\bullet} + CH_3^{\bullet}$	0,3141
$(OH)_3Si^{\bullet} + CH^{\bullet}{}_2\text{-}CH_3$	0,2411

As we can see from the table, the more preferable destruction way from the silica surfaces is the abstraction ethyl-radical, connected through the oxygen atom. Besides, it is necessary to note that the dehydrogenation occur 3,57 time easy from β-carbon then from α-one. It is also has been agreed with experimental predictions. [1]. It was confirmed by this calculation that the oxyradical, which have been obtained by the CO molecule abstraction extracts the H atom from CH_3-group of the CH_2-CH_3 fragment, but not from CH_2-group, in spite of this channel more profitable according to thermo chemistry. All of these predictions are coinciding with experimental observations [4] and spectroscopic facts [2]. The ethyl-radical also can abstract from the deoxygenated surface. It was noted also that the increasing of the hydrocarbon chain has diminished the destruction energy from the surface.

1.Radtsig V.A., Kinetica i catalysis (Russian). 43, №4, P. 539 (2002)
2.Pakansky J., Brown D.W., Chang J.S., J.Phys.Chem. 1981, V. 85. № 17. P.2562

A novel improvement for the molecular graphs matrix calculation and its application in the QSAR studies

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Nowadays the molecular graphs theory built on the topology and graphs theory main principles is successfully used in the QSAR studies. Today we know quite a lot of different molecular graphs invariants.

The famous Shannon formula is used for molecular structure information contents calculation:

$$IC_k = -\sum_i p_i \log_2 p_i \tag{1}$$

which is successfully applied for molecular complexity analysis of the homogenous graphs representing homonuclear skeletons.

Heteroatom molecular graph analysis on the basis of the scheme given above is made by means of the molecular graph marking in such a way that the equivalent vertexes become non-equivalent. It can be achieved by means of the vertex- and edge-weighted graphs. One of the most successful vertex- and edge-weighted graphs indices is the Rouvray index R:

$$R = \sum_i d_{ii} + \sum_{i \rangle j} d_{ij}\,, \tag{2}$$

In formula (2) d_{ii} and d_{ij} are diagonal and non-diagonal distance matrix elements for vertex- and edge-weighted graphs.

In practice it is very important to describe the homogenous and heterogeneous graphs by means of one scheme. For this purpose we have suggested introducing the index of the molecular graph complete complexity.

$$RIC_k = \alpha R + (1-\alpha) IC_k\,, \tag{3}$$

where α is the molecular graph heterogeneity degree.

In that way the new model was originated permitting us to account the influence of molecular chaos generated by the mutual disposition of the atoms in the space as well as by the different nature of these atoms. In particular the structure-property correlations were investigated at different systems. The equilibrium characteristics such as adsorption heat, the Gibbs potential, the Henry constant and gas-chromatographic retain index are analyzed as the properties. They are calculated for different substances adsorption from the gaseous and liquid phases on the active carbon, graphitized thermal carbon black and Silipore 600. Substances with different molecular graphs – homogenous, heterogeneous and graphs with cycles are researched. Thus the obtained data let us declare that with the help of information-theoretic indices on the experimental data for the reference substance group it is possible to predict the equilibrium adsorption characteristics for a number of substances, whose molecular structure can be described by means of molecular graphs of one type.

The method mentioned above was used by us for the molecular graphs matrix analysis either by means of the distances matrix or of graph vertexes contiguity matrix. The Wiener matrix application for alkanes is widely known however this matrix can't be used for the combined molecule analysis of the organic substances belonging to different homological series. The Wiener matrix application range can be widened for structure analysis of different molecules. For this purpose we suggest considering the characteristic polynomial of the distance matrix, the elements of which should be defined as the Rouvray matrix elements. Here the characteristic polynomial or the matrix graph spectral moment is considered as a graph invariant.

β-Cyclodextrin inclusion complexes with methyl xanthines. Molecular mechanics study accounting for the solvent

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Molecular incapsulation of compounds with biological activity by water-soluble and naturally available hosts such as β-cyclodextrin (β-CD) covers a variety of different interests, from structural investigations of non-covalent interactions (including enzyme models) to industrial exploitation. Established applications of β-CD inclusion complexes concern the pharmaceutical industry, and are aimed at improving the bioavailability of barely water-soluble drugs, increasing their stability and reducing unwanted side-effects [1]. N-methylated xanthine derivatives 1,3-dimethyl-xanthine (theophylline, Tp), 3,7-dimethyl-xanthine (theobromine, Tb), and 1,3,7-trimethylxanthine (caffeine, Cf), are well known and widely used drugs. However, Tb is almost unsolvable and solutions of Cf and Tp are relatively unstable at normal temperature [2]. So their inclusion complexes with β-CD are of great interest for pharmacology and medicine.

Four main points are to be clarified in the study of inclusion complexes: proof of actual inclusion, stoichiometry, association constant, and geometry of the complex. Both stoichiometry and the association constants for β-CD inclusion complexes with Tp, Tb and Cf in water solution are known from experiment [2]. Recently, we have simulated the β-CD inclusion processes with above compounds by molecular mechanics calculations *in vacuo* [3]. For each drug molecule, there was shown the possibility to form four types of stable complexes with partial inclusion of the guest into β-CD macrocycle cavity: with imidazole fragment entered into the wider or narrower rim of the macrocycle (A_W- or B_N-complexes, respectively) or with pyrimidine fragment entered into the wider or narrower rim of the macrocycle (B_W- or A_N -complexes, respectively). According to our calculations, A_W-complexes were the most stable. The calculated values of complex stabilization energies correlate with experimental values of complex formation constants [2] as well as with dipole moments of the guest molecules calculated by AM-1.

The aim of the present study was to estimate relative stability of the above inclusion complexes taking into account the effect of water solution. The calculations were carried out using Allinger's MM2(91) force field. Bond dipole approximation was used for electrostatic interactions. For each drug molecule, A_W-complex obtained earlier [3] was placed in a periodic box containing 196 water molecules. These molecular systems were then gently minimized [4]: at first, solute was fixed and solvent was minimized, and then the whole system (including solute and solvent) was minimized. The systems were optimized untill the value of root mean square gradient for total energy was less than 0.005 kcal / (Å mol).

Effect of solvent and polar properties of the guest molecules on relative stability and geometry of the supramolecular complexes, as well as interplay of different contributions to total potential energy of the host-guest supramolecular systems are discussed.

1. Szejitli J. // Med. Res. Rev.–1994.- V.14, №3.- P.353.
2. Wei Y.L., Ding L.H., Dong C. et al. // Spectrochim Acta A. Mol. Biomol. Spectrosc.- 2003.-V.53 (12).- P. 2697.
3. Lisnyak Yu.V., Gubskaya A.V./ Problems of Biological and Medicinal Chemistry.- I Ukrainian Sci. Conf. – Proc. Conf.- Kharkov, 2004. -P.98.
4. Leach A.R. Molecular Modeling/Principles and Applications. – Addison Wesley Longman Ltd. – 1996.- 598 p.

The collectivity of multi-configuration states

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The collectivity of N-electron wavefunctions is a somewhat ambiguous notion, and its concrete definition deserves close attention. The collectivity should quantitatively characterize the participation of excited configurations in a given state vector $|\Psi\rangle \equiv |\Psi(1...N)\rangle$. As commonly assumed, $|\Psi\rangle$ is represented by a series over all k-fold excited configurations ($0 \le k \le N$) with respect to a reference determinant $|\Phi\rangle$. In the simplest approach we define the collectivity index N^{av} by the average k-fold excitation measure $\langle k \rangle$

$$N^{av} \equiv 2\langle k \rangle = 2\,\mathrm{Tr}\,(I-\rho)\,D_1^{\Psi} \qquad (1)$$

where ρ and D_1^{Ψ} are the reference Dirac-Fock density matrix and the first-order density matrix for $|\Psi\rangle$, respectively. With some variations this collectivity measure was used in [1,2].

The present report establishes a close connection of (1) with the collectivity index recently proposed in [3], and compares these indices with the unpaired electron index presented in [4] and related works. Further, an elementary collectivity measure is proposed on the basis of reference coefficient c_0. The corresponding index

$$N^{c0} = -8\ln|c_0|/\ln 2\,, \qquad (2)$$

as well as the index (1), can be interpreted as twice the average number of broken bonds. The theory is exemplified with full CI calculations on atomic and molecular systems in their ground, excited and dissociated states. Several direct and approximate calculations for the CCD and CCSD models are discussed.

1. A.V. Luzanov, O.A. Zhikol, Int. J. Quant. Chem., **105**, No2 (2005).; http://qcc.ru/~fock/proceedings2004/913.
2. A.V. Luzanov, Kharkov University Bulletin, 2004, №626, Chemical Series Issue. 11 (33).
3. M. Head-Gordon, Chem. Phys. Lett., **372**, 508 (2003).
4. K. Takatsuka, T. Fueno, K. J Yamaguchi, Theor Chem Acta, **48**, 175 (1978).

Automated generation of the diagrams and computer code for the state-specific multireference coupled cluster theory.

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The contemporary single reference (SR) coupled cluster (CC) theory is most popular non-empirical quantum chemical method for small and medium size molecular systems. It was demonstrated on the numerous occasions that the CC method with single and double excitations (CCSD) reproduces very well experimental data as well as results of other high-accuracy theoretical methods.

Since SR-CCSD is based on a single determinant reference function it becomes less accurate if the wave function shows a multireference (MR) character. The most typical examples of such situations are chemical bond breaking (or significant stretching), quasidegeneration and electronic excitations. This has led to the explicit use of restricted small set of determinants as the reference functions (MR-CC theory). One of perspective MR-CC approach is based on the *state-specific* (or *state-selective*) SS ideology, where the separate calculation is carried out for each considered state of the system. We proposed the variant of such method (CASCCSD):

$$\left|\Psi_{\text{CASCCSD}}\right\rangle = e^{\hat{T}_1+\hat{T}_2}(1+\hat{C})\left|0\right\rangle,$$

where the operator $(1+\hat{C})$ generates the superposition of the reference states (model space) and the $e^{\hat{T}_1+\hat{T}_2}$ generates the excitations outside the model space. $\left|0\right\rangle$ is so-called formal reference wave function.

Due to the complexity of the algebraic manipulations involved in deriving the CASCCSD equations the method for automated generation of the CC diagrams, algebraic equations and corresponding computer code has been developed [1]. In our method we use the compact *matrix representation* for the *diagrams*. It provides a straightforward procedure for the generation of all necessary topologically nonequivalent diagrams by using simple operations.

Some numerical tests were performed for H_4 and H_8 models in minimal basis set with different degree of degeneracy. For several small molecules (BH, FH, LiH, Li_2, H_2O, N_2) dissociation curves were calculated. The presented automated generated CASCCSD model provides the energies of states very close to the full configuration interaction results.

1. D.I.Lyakh, V.V.Ivanov and L.Adamowicz // *J. Chem. Phys.* -V.122. 024108 (2005).

Quantum chemical study of structure, properties and structural changes of some triazenes, azo- and bis-compounds

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Balancing geometry of triazenes molecules R-C_6H_4-NH-N=N-C_6H_4-NO_2 (where R – H, p-CH_3, o-CH_3, m-CH_3, p-Cl, and p-Br) and their isomeric forms R-C_6H_4-N=N-NH-C_6H_4-NO_2 were studied in this work by non-empiric method of Harty-Fock-Roothan with use of program GAMESS [1] and basic set 3-21G**. It was estimated that izo-form in gas phase is more advantageous energetically.

The complexes of molecules of triazenes with solvent molecules were regarded. It was demonstrated that at change from free molecules to the intermolecular complexes with molecules of polar solvents (two molecules of water or one molecule of acetonitryl or formamide) the difference in energy of common and izo-phorm of triazens somewhat increases. The same situation was observed in calculation of continual model PCM. The mechanism of transformation of common form of triazenes into izo-form in water medium is proposed. It suggests synchronic exchange by the hydrogen atoms between molecules of triazones and water.

Spatial structure and energetic characteristics of the molecules of azo- and bis-azocompounds p-H_2N-C_6H_3(R)-N=N-C_6H_4-NO_2 and O_2N-C_6H_4-N=N-C_6H_3(R)-NH-N=N-C_6H_4-NO_2 (with izo-forms including), where R – H, o- and p-CH_3 were estimaded. Possible content of solvate complexes of these compounds with molecules of solvents, produced due to hydrogen bounds with polar groups was regarded. It was estimated that hydratic envelope of the molecules of azocompounds consists of six molecules of water. The influence of the amounts of solvent molecules in complex and their spatial structure on energetic stability was studied.

Electronic absorption spectra of the azo- , bis-azocompounds and triazenes were calculated by the method of configurational interaction with taking into account only one-electronic exiting. The spectral shifts caused by solvent molecules were estimated.

The spatial structure and relative energetic stability of diazo-cations R-C_6H_4-N(+)≡N, and NH(+)(-C_6H_4-NO_2)(R-C_6H_4-N=N-)(O_2N-C_6H_4-N=N-), which are able to act as intermediates into reaction R-C_6H_4-NH-N=N-C_6H_4-NO_2 + O_2N-C_6H_4-N(+)≡N → O_2N-C_6H_4-NH-N=N-C_6H_4-NO_2 + R-C_6H_4-N(+)≡N were investigated.

The study showed that creation of three-nuclear cation-intermediate in gas phase is energetically advantageous process and its disruption needs only small amounts of energy. The most strong bounds were observed between diazo- cathode ion and two molecules of water and between cation-intermediate and four molecules of water. It was found that solvatation could influence strongly on energetic of studied process.

1. M.W. Schmidt, K.K. Baldridge, J.A. Boatz, S.T. Elbert, M.S. Gordon, J.H. Jensen, S. Koseki, N. Matsunaga, K.A. Nguen, S. J. Su, T.L. Windus, M. Dupuis, and J.A. Montgomery. General atomic and molecular electronic - structure system: Review // J. Comput. Chem. – 1993. – 14, N 11. – P.1347-1363.

Electron properties of oxygen complexes of ferrous ion center

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As was shown by Panov with co-workers oxo ferrous-ion center (so-called alpha center) in FeZSM5 zeolites represents under most conditions [1]. In the present work the reactivity of alpha center is studied by quantum-chemical means. We suggest that the reactivity of this center is determined by the specific electron structure of the [*FeO*] (ferril) moiety of alpha center. The [*FeO*] is modeled by $OFeOH_2$ species.

The problem is tackled by combining CASSCF theory followed by multi-reference perturbation theory (MRMP2) correction with unrestricted DFT supplemented by original analysis of spin-contaminated solution in terms of idealized valence structures [2,3].

As predicted at all used levels of theory two low-lying states can represent the ground state of the [*FeO*] unit: $^5A_1$ and $^5B_2$. the later state appears to be unrestricted DFT solution with one active spin-contamination-determining pair of orbitals which happen to be π_y and π_y^* orbitals in this case. The S^2-exapantion technique allowed us to represent the $^5B_2$ solution as weighted sum of $(\pi_y)^{\downarrow\uparrow}(\pi_y^*)$, $(\pi_y)^{\downarrow}(\pi_y^*)^{\uparrow}$ and $(\pi_y)(\pi_y^*)^{\downarrow\uparrow}$ with quite large weight of the split-electron-pair configuration $(\pi_y)^{\downarrow}(\pi_y^*)^{\uparrow}$. It is this configuration that seems to be responsible for the activity of the [*FeO*] moiety towards the activation of the C-H bond since it allows cycloaddition-type transition state [4]. At the decreased (H)O-Fe-O(H) angles the $^5B_2$ becomes the ground state making [*FeO*] active in the oxidation reactions.

Therefore, the activity of various oxo ferrous species in zeolites can be varied by the form of ferrous ion stabilization (in cationic position, in some defects of zeolite lattice and so on). Which determines in fact the angle O-Fe-O.

1. G.I. Panov, A.K. Uriarte, M.A. Rodkin, V.I. Sobolev, *Catal. Today*, **41**, 365 (1998)
2. I. Zilberberg, S.Ph. Ruzakin, *Chem. Phys. Lett.*, **349**, 165 (2004)
3. I. Zilberberg, S.Ph. Ruzakin, S. Malykhin, G.M. Zhidomirov, *Chem. Phys. Lett.*, **394**, 392 (2004)
4. A. Fiedler, D. Schroder, S. Shaik, H. Schwarz, *J. Am. Chem. Soc.*, **116**, 10734 (1994)

Computer simulation of target-ligand interactions

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The investigations of molecular mechanisms of target-ligand interactions are necessary for understanding of the drugs pharmacological activity. The efficacy of the drug action on the molecular level or the specifity of its interaction with the target biopolymer molecule is evaluated by shape complementarity of their interacting parts and by presence of forces (electrostatic, van der Waals, hydrophobic), allowing to determine the energetic preferability of simulated systems.

The objective of the carried out research work was to investigate the complexation of the double stranded polyribocytidylic acid poly*r*C (target, Fig1) with the analogue of anticancer antibiotic actinomycin D - ActIII (ligand, Fig.2) by means of molecular docking and Monte Carlo method. The double stranded polyrC is a convenient model of nucleic acids serving as targets for many anticancer drugs.

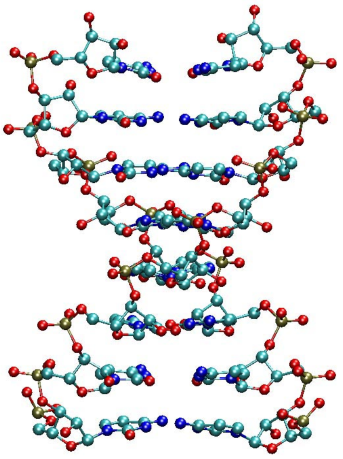

Fig.1. The structure of double stranded poly*r*C

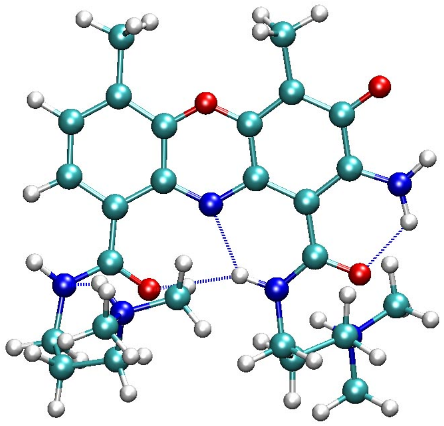

Fig.2. The optimized structure of ActIII

The structure of double stranded poly*r*C was built relying on the known X-ray diffraction analysis data. The partial charges on the atoms of poly*r*C pair and ActIII were calculated using semi-empirical quantum chemistry method pm3. The structures of poly*r*C and ActIII were minimized first *in vacuo* and then in the water (model TIP3P) in the framework of force field AMBER 96. These structures were then used for the generation of poly*r*C-ActIII complexes by molecular docking method (program package AutoDock 3.05). The choice of the most probable structures from the complexes obtained was carried out using UV-spectrophotometry and Raman spectroscopy data concerning hydrogen bond formation between donor-acceptor groups of poly*r*C and ActIII.

Relying on the analysis of molecular docking results and experimental data the five most probable complexes were selected that satisfied following selection criteria: the calculated energies of target-ligand interaction were minimal; the formation of maximum number of hydrogen bonds between donor-acceptor groups of poly*r*C and ActIII was possible; the groups of cytosine and/or oxygens of the poly*r*C sugar-phosphate backbone and NH_2-group of phenoxazone chromophore of ActIII participated in hydrogen bonding.

The influence of solvent – water molecules on the structure of complexes obtained using molecular docking method was determined by means of Monte Carlo method. The simulation was carried out taking into account 800 water molecules. It was shown that water molecules could stabilize in addition complexes of polynucleotide target and ligand forming bridges between their donor-acceptor groups.

MNDO calculations on oxygen evolution at PbO_2 electrode

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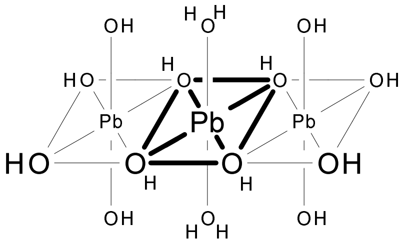
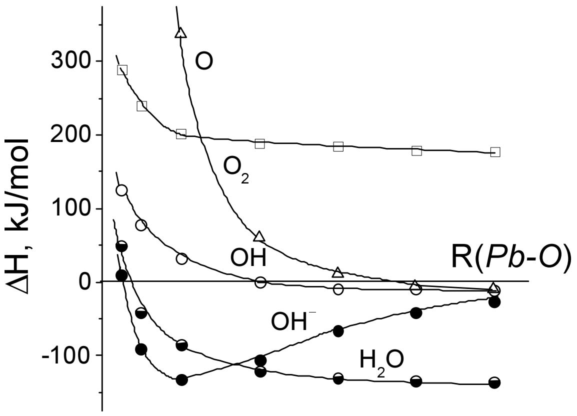
Using the MNDO method, we simulated the process of O_2 evolution on a PbO_2 electrode. Accordingly to the crystallographic data, the coordination numbers of plumbum and oxygen atoms in β-PbO_2 equal to 6 and 3 respectively. As the simulation of the PbO_2 surface by $PbO_5(OH)^{7-}$ or $Pb(OH)_6^{2-}$ models is not sufficiently appropriate by reason of the low coordination number of oxygen atoms that we have utilized more complicated model $Pb_3(OH)_{12}(H_2O)_2$:



Adding two molecules of H_2O instead of OH^- ions allowed to reduce a total charge of system up to zero that is convenient at the analysis of charging and orbital interactions. In this model the central plumbum ion is surrounded by 6 oxygen atoms with coordination number 3. After complete optimization of the geometrical sizes of a cluster under condition of its greatest symmetry the Pb-O bond distance come to 0,220 nm (for comparison, in a cluster $Pb(OH)_6^{2-}$ the Pb-O bond distance is 0,213 nm and in $Pb(OH)_4(H_2O)_2$ - 0,236 nm). Simulating of the process of O_2 evolution was founded on so-called "electrochemical oxide path" mechanism: $2H_2O \rightarrow 2OH^-$ (anion) $\rightarrow$ 2OH(radical) $\rightarrow$ 2O(biradical) $\rightarrow O_2$. Therefore two adjoining species (see boldface lines in figure) take part in the oxygen evolution process:

$$\begin{aligned}
Pb_3(OH)_{12}(H_2O)_2 &\rightarrow Pb_3(OH)_{12}(OH^-)_2 + 2H^+,\\
Pb_3(OH)_{12}(OH^-)_2 &\rightarrow Pb_3(OH)_{12}(OH^{\cdot})_2 + 2e,\\
Pb_3(OH)_{12}(OH^{\cdot})_2 &\rightarrow Pb_3(OH)_{12}(O)_2 + 2H^+ + 2e,\\
Pb_3(OH)_{12}(O)_2 &\rightarrow Pb_3(OH)_{12}O_2 + 2H^+,\\
Pb_3(OH)_{12}O_2 &\rightarrow Pb_3(OH)_{12}(\text{vacancy}) + O_2.
\end{aligned}$$

As we did not simulate the solvation shell of cluster that the complete path of electrochemical reactions was not investigated. In this study only foregoing final states of PbO_2 cluster were calculated. Results of MNDO calculations are shown below as the comparison of cluster's heat of formation (ΔH) with interatomic distance between central Pb atom and oxygen species:



An analysis of the energy parameters for evolution of O_2 from H_2O within the limitations of the simplified PbO_2 cluster model suggests that weak interaction between oxide and oxygen species is the most essential parameter that is influenced by electronic properties of the very oxide.

Potential antimicrotubular activity of anticancer compound cyproterone acetate

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Cyproterone acetate (CypA), active steroid component of anticancer drug Androcur, binds highly competitively with dihydrotestosterone at androgen receptor sites. Respectively, we also can assume its ability to directly interact with tubulin molecules and, thereby, to possess by antimicrotubular activity, because this property is common for other steroids (particulary for antitumor estradiols) earlier [1, 2]. To verify this hypothesis the spatial structure of CypA by *ab initio* method with using medium basis set was reconstructed. This structure was compared it with molecular structures of different antimicrotubular compounds. It was shown that features of spatial structure and electron properties of ring D of CypA molecule with attached side groups have analogues in the spatial structure of taxol. This well-known compound interacts with β-tubulin molecule that results in irreversible stabilization of microtubules. To check taxol-like activity of CypA we reconstructed spatial structure of its complex with human β-tubulin by manual docking CypA molecule into taxol-binding site on β-tubulin surface and computed molecular dynamics of complexes “tubulin-CypA” and “tubulin-taxol”, and also free CypA and taxol molecules, using GROMACS software (*ffgmx* force field) for 10 ns time interval. Comparative analysis of obtained data has clearly revealed similar behavior features of both ligands. Average values of conformational energy of ligands in binding state have been fundamentally decreased in comparison with their free state – for 175 kJ/mol in CypA case and for 250 kJ/mol in taxol case – that testifies about very high stability both complexes in time. Thus, we can assert that cyproterone acetate really possesses by affinity to β-tubulin molecule and can interact with tubulin in taxol-like mechanism.

1. *Verdier-Pinard P., Wang Z., Mohanakrishnan A. K., Cushman M., Hamel E.* A steroid derivative with paclitaxel-like effects on tubulin polymerization // Mol. Pharmac. – 2000. – V. 57. – P. 568-575.
2. *Nyporko A.Yu., Stakhovsky A.E., Stakhovsky E.A., Blume Ya.B.* The structural dependence of the switching of estradiol antitumor effects from the action mechanism destabilizing microtubules to that stabilizing ones // Rept. Natl. Acad. Sci. Ukraine. – 2005. – N 5. – P.155-160 (in Russ.).

The quantumchemical investigation of the heterocyclization process of N-sulfonylsubstituted endo-5-aminomethyl-exo-2,3-epoxybicyclo[2.2.1]heptanes

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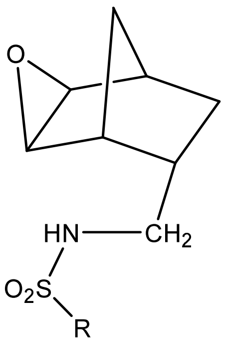
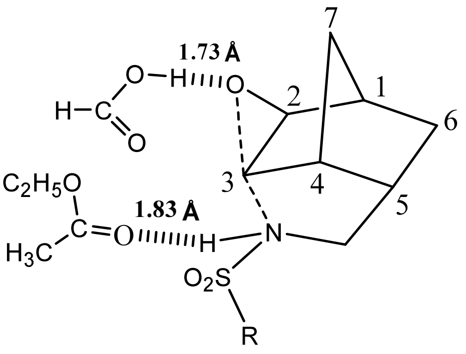
The tricycle azabrendanes as potential biologically active systems recently become the objects of increase attention but the regularities of their formation practically have not been investigated. From the experimental results it is known that these derivatives as well as the sulfonamides of the epoxynorbornane row (I a-o) are the products of oxidation of endo-5-aminomethyl-exo-2,3-epoxybicyclo[2.2.1]hept-2-en by peroxyphthalic acid.

In this work the potential energy surface (PES) of the heterocyclization process has been investigated by semiempirical quantumchemical method PM3 and by Density Functional Theory (BHandHLYP/6-31G(d)). The influence of solvent has been taken into account by the COSMO, PCM and Onzager models. The transition states (II a-o) have been located on the PES of reactions. Values of the corresponding activation barriers have been calculated relatively to prereaction complexes.



(Ia-o)



(IIa-o)

where R=CH_3(a), CF_3(b), C_6H_{11}(c), C_6H_5(d), o-$NO_2C_6H_4$(e), m-$NO_2C_6H_4$(f), p-$NO_2C_6H_4$(g), p-$CH_3C_6H_4$(h), o,p-2$NO_2C_6H_3$(i), o-NO_2,p-$CH_3C_6H_3$(j), o-CH_3,p-$NO_2C_6H_3$(k), o-OCH_3,m''-$NO_2C_6H_3$(l), o,p-2ClC_6H_3(m), m,p-2ClC_6H_3(n), o-NO_2,p-ClC_6H_3(o).

The results of calculations has shown, that the transition states (II a-o) are S_N2-like (it could be seen from the values of the bond angles OC^3N) and have a late character ($r(OC^3)>r(C^3N)$). The obtained results confirm the significant importance of electron factor in proceeding of the process of heterocyclization: introduction to benzene ring of electron-acceptor substituents, such as NO_2-groups, increase activation energy, meanwhile the electron-donor substituents, such as CH_3-groups, decrease them. In addition we have shown the importance of steric factor: investigation of cyclohexyl derivative (Ic) and the compounds, containing two substituents in benzene ring, has shown the increasing of activation energy in comparison with those derivatives, which have smaller substituents.

Comparative analysis of that data, which where obtained in calculations with consideration of different solvents (ethylacytate and chlorophorm) has revealed an essential influence of the character of medium on proceeding of the process, especially – the importance of specific solvatation. The received values of activation energy allowed as arrange the compounds in the following row:

I b> I i> I e> I c> I k> I o> I j> I a> I l> I f> I m= I n> I g> I d> I h,
which is in a good agreement with experimental data.

Ab initio calculations of X-F spin-spin coupling constant and ^{19}F NMR chemical shift for PF_6^- and AsF_6^- anions

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Complex fluoride salts with hexafluorophosphate PF_6^- and hexafluoroarsenate AsF_6^- anions can be used as an active part of electrolytes in rechargeable lithium cells and supercondensers. Since electrolytes are multicomponent systems, a comparison of the calculated values of the spin-spin coupling constant and ^{19}F chemical shits with experimental data is the only way to reliably assign NMR signals to the corresponding nuclei.

Here we present HF and DFT study of NMR spectra parameters of PF_6^- and AsF_6^- anions. $J_{P,F}$ and $J_{As,F}$ values have been calculated using standard 6-31G, 6-31++G(2d,2p), 6-31++G(2df) and recently developed [1] magnetically consistent 6-31G$^{\#\#}$ basis sets (Table). ^{19}F NMR chemical shift values were calculated at HF/6-31G$^{\#\#}$ level of theory.

Table. Calculated P-F and As-F nuclear spin-spin coupling constants J (Hz)

Molecule	Method	Basis set	Number of basis functions	J_{calc}	$J_{exp.}$
PF_6^-	RHF	6-31G	67	541	708[2]
	B3LYP	6-31G	67	950	
	RHF	6-31++G(2d,2p)	179	377	
	B3LYP	6-31++G(2d,2p)	179	762	
	RHF	6-31G$^{\#\#}$	163	200	
	PCM/RHF	6-31G$^{\#\#}$	163	203	
	B3LYP	6-31G$^{\#\#}$	163	696	
	PCM/B3LYP	6-31G$^{\#\#}$	163	698	
AsF_6^-	RHF	6-31G	78	595	935
	B3LYP	6-31G	78	1207	
	RHF	6-31++G(2df)	239	481	
	B3LYP	6-31++G(2df)	239	1140	
	RHF	6-31G$^{\#\#}$	207	297	
	PCM/RHF	6-31G$^{\#\#}$	207	300	
	B3LYP	6-31G$^{\#\#}$	207	898	
	PCM/B3LYP	6-31G$^{\#\#}$	207	901	

Obtained values of ^{19}F chemical shifts (-72.2 and -62.8 ppm for PF_6^- and AsF_6^-) are in excellent agreement with experimental values (-72.4 [2] and -64.8 ppm correspondingly).The results are derived clearly demonstrate the importance of taking into account electron correlation for the calculations of spin-spin coupling constants and advantages of physically justified 6-31G$^{\#\#}$ basis set over the standard ones. All calculations performed by the G03W package of program[3].

1. V. V.Rossikhin, S.I.Okovytyy, L.I.Kasyan, E.O.Voronkov, L.K.Umrikhina, J. Leszczynski *J. Phys. Chem.* A. **2002**, *106*, 4176.
2. A.V.Plakhotnyk**,** L.Ernst, R.Schmutzler**.** *J.Fluorine Chem.,* **2005,** 126, 27**.**
3. M. J. Frisch, G. W. Trucks, H. B. Schlegel, et al., Gaussian, Inc., Wallingford CT, **2004**.

AIM electron density analysis on the structure and bonding in alicyclic olefins and oxiranes

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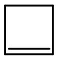
The cyclic olefins and epoxides are perspective syntons in production of the medicine and polymer matherials. Strain and polarity are provided them the wide spectra of transformation with nucleophilic and electrophilic reagents. The electronic and geometrical structure of organic molecules is the basis for investigation of the reactivity of organic compounds.

The atom in molecules (AIM) approach has been employed to calculation of the electron density distribution of alicyclic olefins (1-8), epoxides (9-17), ethylene and oxirane molecules.



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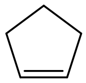

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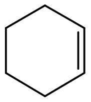

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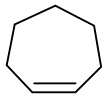

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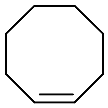

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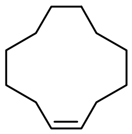

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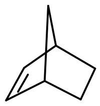

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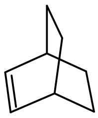

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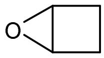

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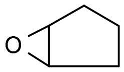

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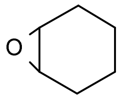

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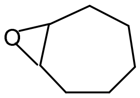

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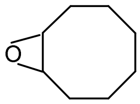

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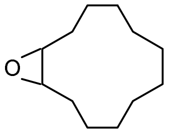

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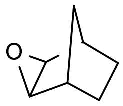

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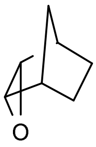

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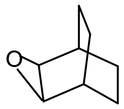

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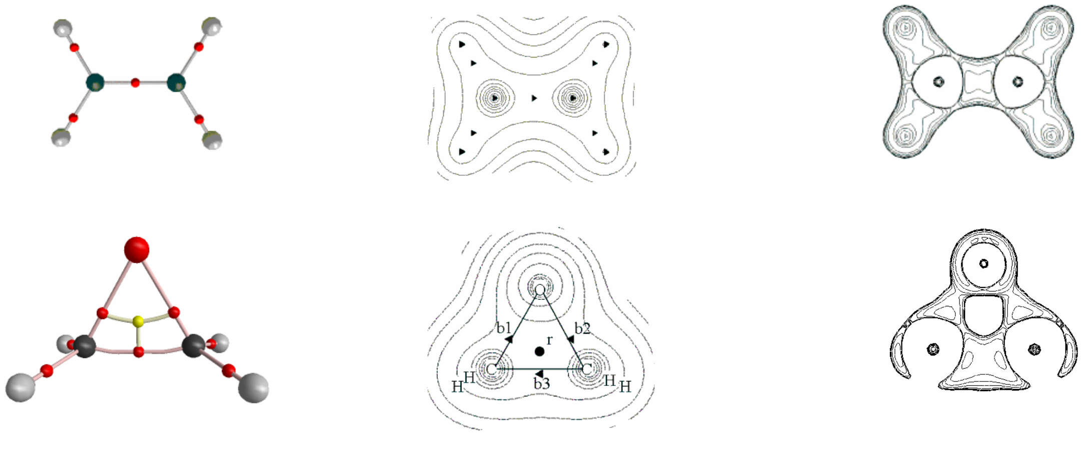
The calculations have been performed at the PBE1PBE/6-31+G* level of theory. The properties of bond and ring critical points, charge density, the Laplacian of the charge density for alicyclic olefins and epoxides have been investigated and compared with those for ethylene and oxirane corresponding (Fig.1).



a b c

Fig. 1. Molecular graphs (a), contour maps of the charge density (b), the Laplacian of the charge density (c) for ethylene and oxirane

The analysis of the structures and bonding of above mentioned compounds rows has been carried out. Thus strength and ellipticity of C=C, C-C and C-O bonds, surface delocalization electron density, π–character of the epoxidic ring have been compared. The topology of the electron density of several olefins and epoxides show the existence of closed-shell interaction between hydrogen atoms attached to nondonding carbon atoms.

Structure of O–N–Y amides: nitrogen pyramidality and anomeric effects

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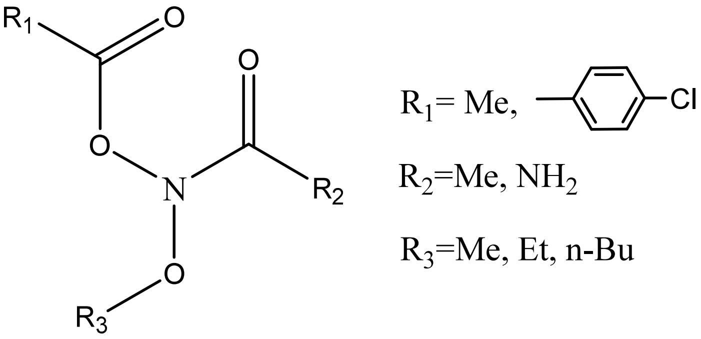
"Anomeric" amides, which contain two oxygen substitutents at nitrogen, have strongly different properties compared to "classical" amides. Recently [1] it was found that in N-acyloxy-N-alkoxybenzamides amide nitrogen atom has substantially pyramidal configuration with the sum of bond angles centred on the atom of 324°. This results in high carbonyl stretch frequencies (1720-1740 cm^{-1}) and low amide isomerisation barriers.



R_1= Me,

R_2=Me, NH_2

R_3=Me, Et, n-Bu

In this work we have performed X-ray diffraction study of the series of ureas and carbamates. Our results reveal highly pyramidal configuration of the amide nitrogen in the O-N-O fragment (the sum of bond angles of 329-336°). Two types of conformations were observed in crystal with carbonyl group of acyloxy-substitutient oriented towards front or rear side of the lone pair of amide nitrogen atom. Analysis of bond lengths demonstrates considerable differences in the N-O bond lengths. The N-OC(O)R bond (1.424(2)-1.447(2) Å) is much longer than N-OAlk bond (1.396(2)- 1.402(1) Å) reflecting the presence of $n_{O(R)} \rightarrow \sigma^*_{N-Y}$ anomeric interactions in O-N-O group. In order to get more detailed information about the factors determining molecular structure of such amides we have performed the quantum-chemical calculation of the set of O-N-O "anomeric" amides at the DFT, MP2, CASSCF and CCSD levels of theory.

Our results show that the conformations observed in crystal are the most stable for particular molecules. Analysis of the wave functions in terms of NBO theory shows that the main stabilizing factors are $n_{O(R)} \rightarrow \sigma^*_{N-Y}$, $n_{O(Y)} \rightarrow \sigma^*_{N-O(R)}$ and $n_{O(R)} \rightarrow \sigma^*_{C-N}$ anomeric interactions found in that conformations. Barrier of the amide nitrogen inversion is considerably lower than in N,N-dialkoxyamines as a result of $n_N \rightarrow \sigma^*_{C=O}$ interaction in transition state. Barrier of C–N amide bond rotation is also decreased due to preservation of hyperconjugation in amid group.

1. A. E. Gillson, S.A. Glover, D. J. Tucker, P. Turner, *Org. Biomol. Chem.*, **2003**, 1, 3430-3437.

Intramolecular hydrogen bonds in canonical 2'-deoxyribonucleotides

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The canonical 2'-deoxyribonucleotides (DNTs) (2'-deoxythymidine-5'-phosphate (pdT), 2'-deoxycytidine-5'phosphate (pdC), 2-deoxyadenosine-5'-phosphate (pdA) and 2'-deoxyguanosine-5'-phosphate (pdG)) are building blocks of DNA macromolecules. Therefore, an investigation of the structure and conformational characteristics of these molecules is very important for understanding the structure of the conformational dynamics and functions of this type of biopolymers.

Recently [1,2] on the basis of the calculations by B3LYP/6-31G(d) method it was demonstrated that conformation of DNTs is additionally stabilized by intramolecular N-H…O and C-H…O hydrogen bonds. However, some of these bonds are rather weak and unconventional. Therefore, we perform detailed investigation of characteristics of intramolecular hydrogen bonds in monoanionic DNTs using B3LYP/6-31++G(d,p) method.

Results of calculations reveal that application of larger and more diffuse basis set lead to complete disappearances of minima on the potential energy surface (PES), which correspond to syn conformers of pdT. In the case of pdC and pdA only one conformer is observed in syn region of the PES with almost orthogonal orientation of nucleobase with respect to furanose ring. Intramolecular N-H O hydrogen bond between amino and phosphate groups stabilize such orientation of nucleobase. Formation of this hydrogen bond results in significant out-of-plane deformation of pyrimidine ring in cytosine and adenine.

Stable conformers with syn orientation of base are found only for pdG. They are stabilized by intramolecular N-H…O hydrogen bond due to suitable location of the amino group of guanine.

Topological analysis of the electron density distribution using Bader's "Atoms in Molecules" theory reveals presence of several (3,-1) bond critical points which corresponds to intramolecular C-H…O hydrogen bonds for each stable conformer of DNTs. However, detailed analysis of additional criteria for hydrogen bonds (volume penetration, charge transfer etc) within Bader's theory indicates that some of these bonds should be considered rather as electrostatic interactions between closed shell atoms than real hydrogen bonds. These findings agree well with results of calculations of interaction energy between atoms using NBO theory. It is found that (3,-1) critical points with value of electron density below 0.011 au correspond to interaction between two atoms with E(2) energy less 0.5 kcal/mol. Therefore, such interactions should not be considered as hydrogen bonds.

1. O. V. Shishkin, L. Gorb, O. A. Zhikol, J. Leszczynski, J. Biomol. Struct. Dyn. 21 (2004) 537.
2. O. V. Shishkin, L. Gorb, O. A. Zhikol, J. Leszczynski, J. Biomol. Struct. Dyn. 22 (2004) 227.

Interaction of alkali metal ions with the DNA phosphate group

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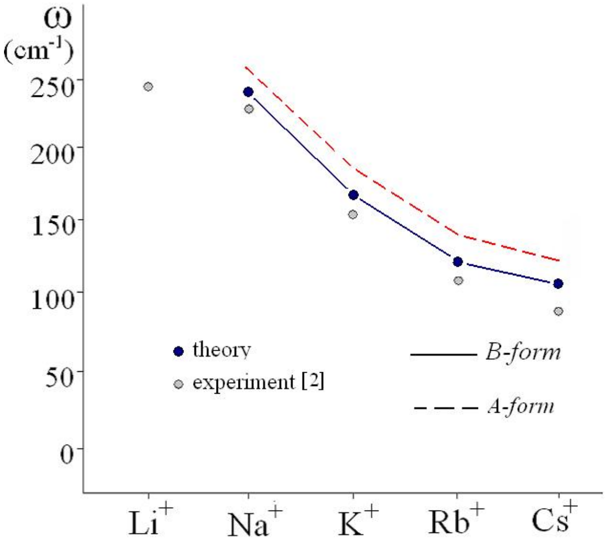
The interactions of the counterions with charged phosphate groups of the DNA backbone determine the conformation of the macromolecule and its mobility in the processes of biological functioning [1]. Counterions with the phosphate groups form the uniform structure that may be considered as an ion lattice. The vibrations of such a system have to be sufficiently intensive and well observed on experimental study. The influence of the counterion species on DNA vibrations reveals themselves in Raman low-frequency spectra [2], but the place of the ion-phosphate mode is not determined yet.

To determine the place of ion-phosphate modes in the DNA low-frequency spectra the model of conformational vibrations of double helix with tethered ions of alkaline metals has been elaborated [3,4]. In frames of this approach the DNA ion-phosphate vibration is considered as a mode of ion crystal. The value of the frequency of such a mode may be determined by the following formula:

$$\omega = \sqrt{\frac{\gamma}{m_a}}\,; \qquad \gamma = \frac{M_\alpha \cdot e^2}{4\pi\varepsilon\varepsilon_0 r_0^3}\left(\frac{r_0}{b}-2\right). \qquad (1)$$



Here m_a is the ion mass, M_α is Madelung constant of the DNA ion-phosphate lattice, e is the ion charge, ε – is the dielectric constant of environment within the phosphate group, r_0 – the equilibrium distance between charges, b is the repulsion constant. All this parameters were estimated in [3,4] and the frequency of ion-phosphate vibrations was obtained.

It was shown that the ion mode lies in frequency range of 90–250 cm^{-1}, and depends on counterion type and double helix form (see figure). Our calculations qualitatively describe the experimental data [2]. To more exact determination of such a frequency it should be useful to estimate the ion vibration constant (1) more exactly.

1. L.D. Williams, L.J. Maher III // Annu. Rev. Biophys. Biomol. Struct 29, 497 (2000).
2. T. Weidlich, J.W. Powell, L. Genzel, A. Rupprecht // Biopolymers 30, 477 (1990).
3. S.M. Perepelytsya, S.N. Volkov // Ukr. J. Phys. 49, 1072 (2004).
4. S. N. Perepelytsya , S. N. Volkov // Biophysical bulletin, Kharkov, № 2, 2004.

Monte Carlo simulation of the adsorption of simple gases on transition metals and CO oxidation on Pt(111)

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Results from simulations of the adsorption of hydrogen on the (110) surfaces of W and Mo, the structures and adsorption kinetics of oxygen and CO on the Pt(111) surface, and the catalytic reaction of CO oxidation are presented. The choice of these systems is motivated not only by their practical importance and fundamental interest but also by the fact that substantial progress has been made toward understanding the processes of adsorption and the formation of film structures for them with the use of the Monte Carlo method. One of the main requisites for simulation of the adsorbed film structures is to adequately incorporate the lateral interaction between adsorbed molecules, which includes both a direct interaction (electrostatic and exchange) and indirect (via electrons of the substrate). In particular, the correct description of the lateral interaction in the simulation has permitted explanation of the mechanisms of formation of the structures of CO films on platinum. Results of the simulations are in good agreement with experiments, which suggests validity of the concepts of the precursor states in the dissociative adsorption, indirect lateral interaction between adsorbed particles, and reveals important role of mobility of the species in formation of film structures and in reaction between adsorbed CO molecules and O atoms. A new model of catalytic CO oxidation reaction, in which only oxygen atoms in hcp-type threefold adsorption sites on the Pt(111) surface are chemically active, is suggested.

Quantum-chemical calculation of $CuAl_2$ intermetallics interaction with chloride containing water environment

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The current state of development of the electrochemical corrosion theory is characterized by transition from standard phenomenological approaches up to molecular ones. Within the frame of such approach the metal surface is considered not as sets of heterogeneous parts with different electrochemical properties, but as sets of atoms of one or different kinds which are placed in the certain positions of a crystal lattice. In relation to an electrode these atoms have different values of electronic densities the surface being a system of local anode-cathode centres and causing corrosion destruction of metals. The estimation of corrosion dissolution of metals may be developed by consideration of solution ions and water molecules influence on the durability of metal bond with the use of quantum chemical semiempirical calculation and cluster models of the electrode.

The object of our researches was the aluminium alloy of AA2XXX system. In agreement with the X-ray data there on intermetallic phase $CuAl_2$ is present in such alloys. Quantum-chemical calculations were carried out on the cluster $Cu_{10}Al_{32}$ which has a layered tetragonal structure (fig. 1). We investigated adsorption characteristics of interaction of water and chlorine ions with surfaces (100) and (110) of the cluster. Energies of aluminium and copper cations desorption as $[(H_2O)MeCl]^{n+}$ into environment from the surface (110) were also compared. For calculation of geometrical and electronic structure of the intermetallic cluster we used semiempirical method PM3 of the computer package MOPAC [1].

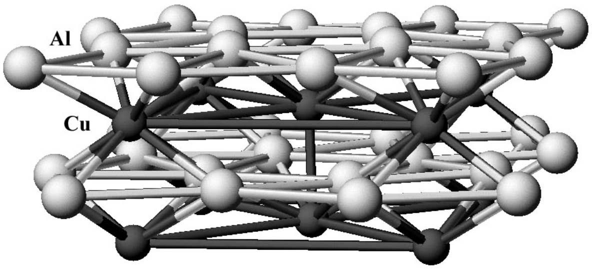

Fig. 1. The cluster $Cu_{10}Al_{32}$

The adsorption heats of water which was adsorbed in atop position on the cluster surface (100) were 0.33 eV and 0.23 eV on the layer of copper and aluminium accordingly. The difference was caused by the contribution of *d*-orbital to the bond: it reached almost 38% for Cu though its band was completely filled up by electrons and was absent for Al. The chloride ion communicates with the layer of aluminium more strongly, because of the negligible contribution of *d*-band of Cu (0.25%) and a sufficient overflow of the ion electronic density to aluminium cluster free zone: 15% for Al and only 0.3% for Cu. Calculations of heats of competitive adsorption of the chloride ion on surface (100), covered with water molecules (on a layer of aluminium – 1.96 eV, on a layer of copper – 1.13 eV) have shown the situation. The most energetically favourable position of chloride ion on the surface of a copper layer is atop, and on a aluminium layer is bridge. The parameters of water and chloride ion adsorption differ at their adsorption sites on the surface (110) of the cluster $Cu_{10}Al_{32}$ which has a stepped structure. The water is adsorbed in atop position on atoms of aluminium with adsorption heat 0.38 eV, the ion of chloride settles down at bridge position over the communication line Al–Cu. Thus heat of adsorption grows up to 2.26 eV. The received results testify that the surface (110) would be dissolved more intensively in Cl^- environment, due to a high adsorption ability of the ion on this surface. Energy of desorption of the $[(H_2O)AlCl]^{n+}$ complex is lower than that of copper complex (2.06 eB, i 3.58 eB respectively).

The calculated adsorption-desorption characteristic on the surface cluster $CuAl_2$ indicates the more intensive dissolution of aluminium from the intermetallic compound because of the formation of local adsorption centres for the system aluminium – copper. So, one may establish about the anode reactions on Al atoms and cathode processes on Cu atoms.

1. Stewart J.J.P. Mopac: a semiempirical molecular orbital program // J. Comput.-Aided Mol. Des. – 1990.– Vol.4, №1.– P. 1-105.

Performance of POLMAG-3 computational program for calculations of static molecular polarizabilities

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The electric dipole polarizability is the basic descriptor of the interaction of the molecular charge distribution with an electric field. Although developing of theoretical approaches for calculations of polarizability was a target of numerous investigations, improvement of computational scheme for such calculations is still of significant interest.

Here we present the results of quantum-chemical calculations of static molecular polarizabilities for number of organic compounds, performed by computational programs POLMAG-3 developed within the framework of the coupled perturbed Hartree-Fock approach based upon the simultaneous analytical dependence of both the bond order matrix and basis set functions on the corresponding perturbation parameters. [1, 2] (Table).

Table. Polarizabilities of molecules in atomic units

Approach	$(CH_3)_3N$	CH_3CH_2CN	CH_3NH_2	$(CH_3)_2NH$
POLMAG-3/HF/STO-3G	53.489	46.127	25.691	39.650
POLMAG-3/HF/6-31G	52.270	44.302	25.146	38.436
HF/6-31G	38.470	32.440	18.041	28.440
PBE1PBE/6-31G	39.960	32.946	18.334	29.276
HF/6-311++G(3d,2p)	47.047	40.054	23.568	35.306
PBE1PBE/6-311++G(3d,2p)	51.194	41.930	25.152	38.008
Experiment	52.52 [3]	42.03 [4]	27.05 [5]	39.79 [3]

Approach	CH_3CHO	$CH_3C(O)CH_3$	$(CH_3)_2CHCN$
POLMAG-3/HF/STO-3G	32.076	45.434	59.684
POLMAG-3/HF/6-31G	30.043	42.04	57.026
HF/6-31G	22.410	32.112	42.574
PBE1PBE/6-31G	23.092	33.051	43.369
HF/6-311++G(3d,2p)	27.960	39.082	51.473
PBE1PBE/6-311++G(3d,2p)	30.151	42.113	54.149
Experiment	30.81 [6]	43.30 [7]	54.34 [4]

A comparison of the calculated and experimental values clearly demonstrates the superiority of the proposed approach with the small-sized STO-3G and 6-31G basis sets over the standard HF and DFT calculations with the 6-31G basis set. In most cases calculations with the new method provide better results if compared to the HF calculations with the extended 6-311++G(3d,2p) basis set.

1. V.V.Rossikhiin, E.O.Voronkov, S.I.Okovytyy, L.L.Shapovalov. *Scientific Israel – Technologacal Advantages*. **2000**, *2*, 35.
2. S.I.Okovytyy, E.O.Voronkov, V. V.Rossikhin, O.K.Balalayev, J. Leszczynski, *J. Phys. Chem., **2004**, 108*, 4176.
3. G.L. D. Ritchie, E.W. Blanch *J. Phys. Chem.* A **2003**, *107*, 2093.
4. G.L. D. Ritchie, E.W. Blanch *J. Phys. Chem.* A **2004**, *108*, 4515.
5. N. J. Bridge, A. D. Buckingham, *Proc. R. Soc. London, Ser. A* **1966**, *295*, 334.
6. V.W.Couling, B.W.Halliburton, R.I.Keir, G.L.D.Ritchie *J. Phys. Chem.* A **2001**, *105*, 4365.
7. M.P.Bogaard, A. D.Buckingham, R. K.Pierens, A. H.White, *J. Chem. Soc., Faraday Trans. 1* **1978**, *74*, 3008.

Modeling of molecular interactions in selected biomolecules

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By the use of *ab initio* method at Moller-Plesset level of theory (MP2) and DFT method, bond lengths and IR spectra are calculated for base pairs - cytosine-guanine, 5-azacytosine-guanine, and in complexes of 5-azacytosine with 5 water molecules and 5-azacytosine with guanine and 8 watermolecules.5-Azacytosine is an important compound used to to cultivate stem cells. It is revealed that the formation of the hydrogen bond characteristics in the pairs and complexes studied are followed by changes in the spatial structure of the nucleic acid component (NAC) molecule at fragments taking part in the formation of these hydrogen bonds and at the adjacent fragments. In the case of the 5azaC+G+8 H2O complex formation values of these changes are the highest.

Interaction energies were calculated for the 5azaC+G+8H2O complex. 23 bands induced by vibrations of the OH groups of water molecules and 15 bands related to the vibrations of the subunit of the complex that consists of guanine (or 5-azacytosine) and selected water molecules are revealed in the high-frequency (2990-3720 cm-1) and low-frequency (20-100 cm^{-1}) regions of the IR spectrum of this complex."

The applied calculation methods - *ab initio* MP2 and DFT theory levels with the 6-31G* basis set permit sufficiently good (to 1% precision) predictions of the bond lengths in the pyrimidine ring, the length of the carbonyl bond in isolated NAC and its change upon the complex formation. These methods describe quite well changes in the frequency of the carbonyl group vibration in the case of the complex formation. On the basis of experimental and calculation data, the carbonyl bond lengths changes were related to the number of the hydrogen bonds. An empirical dependence between the bond length of the carbonyl group and the frequency of its vibration is provided.

By the use of *ab initio* method at Moller-Plesset level of theory (MP2), bond lengths, electron distribution and IR spectra are calculated for complexes of some adenine tautomers with Zn^{2+} ion. Upon the formation these complexes the amino group rotates through 90^0 with the ion attachment at N7 and N1, that is followed with significant changes in the high-frequency region of the spectrum. In the complexes studied an essential transfer of charges occurs, accompanied by redistribution of the electron density on the adenine molecule.

Use of quantum chemical interatomic potential for Monte Carlo simulation of hydrate cover structure for crystalline silica surface

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Physico-chemical properties of high disperse silica are controlled to a considerable extent by the composition and structure of hydroxyl and hydrate shells due to a great specific surface area of SiO_2. The hydrate cover is formed because of binding water molecules with surface hydroxyl groups as a result of the formation of hydrogen bonds or with coordinately unsaturated surface silicon atoms.

As nowadays there are no suitable methods of calculation of the interaction potential water molecules with amorphous solid surface, it is necessary to select a definite face of crystalline silica as a cluster simulated for the surface, the potential for water-water interaction being that well known from the literature.

The main difficulty consists in an approximation of the potential obtained numerically with an analytical one as well as the development of a method for satisfying the frontier conditions compatible with a hexagonal structure of a solid support. Nevertheless, combining these conditions somewhat simplifies the problem and gives an opportunity to diminish the number of water molecules needed for obtaining true results. The curves of the radial distribution of oxygen-oxygen interatomic distance within the hydrate shell in this case can be the experimentally tested properties. Besides, the important information can be obtained via comparing the structure of hydrate shells at silica surfaces for various crystalline modifications.

Turning from quantum chemical calculations to statistical methods, namely to Monte Carlo method, let it possible to reproduce the equilibrium parameters of water films on silica surface along with their macroscopic properties.

The system of $[(Si_6O_{12}\cdot 6H_2O)+50\ H_2O]$ was taken as a model consisting of the cluster simulated for a region of silica surface (111) face and water molecules of hydrate shell. The interaction energy between the cluster and the water molecule was computed by ab initio quantum chemical method with 3-21G basis set and then approximated with a five-parameter function. The water-water interaction energy was calculated within some polarization models of various complexities.

The structure of liquid phase was predicted due to the curves of radial distribution as well as the structure and composition of the clusters of water molecules near surfaces of different silica polymorphs. Estimations were carried out of water molecules binding with surface silanol groups and coordinately unsaturated silicon atoms.

The quantum-chemical analysis of the influence of a glycine ligand on the electroreduction of Cr^{3+} ion

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The results of the analysis of possible mechanism of electroreduction of aquo- and composed monoglycineaquocomplexes in a neutral medium based on the quantum-chemical modeling of charge transfer reaction in a polar medium are given. The quantum-chemical calculations have been performed by means of the GAMESS software complex at UHF/6-31(3d,3p) level of theory. The influence of the hydratation effect has been considered by means of the Kirkwood-Onsager model.

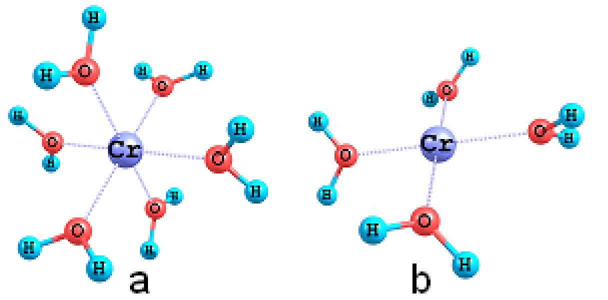

Fig.1. Geometry of a – octahedral aquocomplexes, b - four coordinating aquocomplex

According to the calculation for complexes with +3 an +2 oxidation degree the most stable configuration is octahedral (Fig 1a, 2a), which is in line with the experimental data. While the four coordinating squared flat structure turned out to be more energetically stable for the intermediate aquocomplexes Cr^+ (Fig 1b). In the case of monoglycineaquocomplex the four coordinating squared and three coordinating triangle structures have virtually the same energy (Fig 2b, 2c).

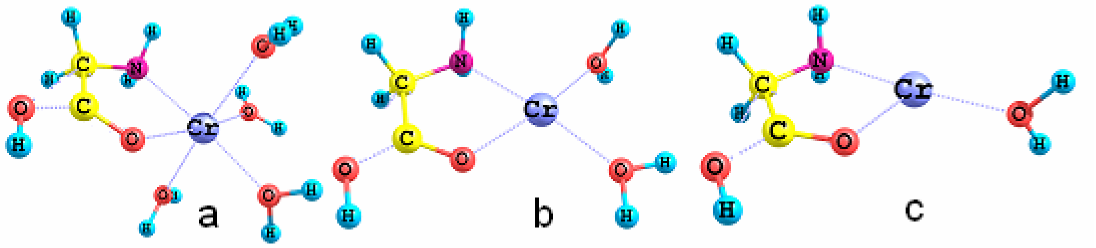

Fig. 2. Geometry of a - octahedral monoglycineaquocomplexes, b - four coordinating monoglycineaquocomplex, c – three coordinating monoglycineaquocomplex

It has been shown, that both octahedral complexes Cr^{3+} (Fig. 1a, 2a) can receive one electron relatively easy in both of the systems and can be reduced to a Cr^{2+} without any essential inner reconstruction. Addition of an electron to octahedral complexes of Cr^{2+} leads to significant increasing of energy of the system. In order to add an electron octahedral complexes of Cr^{2+} have to be transferred to form coordinating states (Fig. 1b, 2b). This transformation requires a great energy consumption. Thus, such a reconstruction as

$$Cr^{2+}\cdot 6H_2O_{aq} \rightarrow Cr^{2+}\cdot 4H_2O_{aq} + 2H_2O_{aq}$$

requires energy to increase by 67,7 kJ/mol. The presence of glycine molecule as a ligand in the system decreases this energy to 49,6 kJ/mol.

The transfer of the third electron does not require pre-reconstruction of the complexes of Cr^+ and it occurs like an barrierless process.

Thus, the transfer of the second electron is the limiting stage of the electroreduction of complexes of Cr^{3+}. The main discharging states in this stage are the flat four (Fig 1b, 2b) or three for glycine systems (Fig 2c) coordinated structures where the glycine's participation decreases the required intrasphere energy of the transformation of the initial octahedral systems.

Influence of substituents on aromaticity of benzene ring in monosubstituted benzenes

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Aromaticity is one of the key concepts in modern organic chemistry. Therefore, quantitative estimation of this phenomenon was a subject of numerous papers. However, only very recently Krygowski et al. [1] tried to estimate influence of substituents on aromaticity degree of benzene ring. They concluded that π-system of benzene ring is highly resistant with respect to substituents effects. This conclusion leads to question about applicability of different aromaticity indexes for estimation of aromaticity of benzene ring in such molecules. Therefore, we performed theoretical studies of aromaticity of benzene ring on monosubstituted derivatives of benzene using structural (Bird and HOMA), magnetic (NICS and its modifications) and recently developed E_{def} index which represent energy of out-of-plane deformation of aromatic ring [2].

Molecular structure of C_6H_5X molecules (where X=H, F, Cl, NH_2, OH, OMe, CN, CHO, $CONH_2$, COOH, COOEt, NO_2, COMe, Me) was optimized at the MP2/cc-pvdz level of theory. Values of NICS0, NICS1 their z-components (NICS-z) and anisotropy of NICS components (NICS-anis) were calculated using HF/6-31+G(d,p) method. Ring deformation energy was obtained by scan of relevant endocyclic torsion angle within benzene ring [2].

Results of calculations demonstrate that structural aromaticity indexes are not able to reproduce substituents effects. Bird and HOMA aromaticity indexes demonstrate very small range of variations without any reasonable agreement with substituent strength. In particular, Bird index indicates the largest decrease of aromaticity degree for methoxy derivative while obviously methoxy group possesses significantly smaller perturbation ability as compared to amino or nitrogen groups.

Similar conclusion should be made for NICS0 and NICS1 indexes. Value of these indexes in some substituted benzenes (R=F,CN) is even higher as compared to unsubstituted benzene. These are obvious artifacts indicating inapplicability of NICS0 and NICS1 for analysis of relatively small variations of aromaticity in monosubstituted benzenes.

The NICS-z and NICS-anis indexes correctly reproduce decrease of aromaticity degree of benzene ring due to presence of substituents. However, they significantly overestimate influence of carbonyl containing groups.

Such problems are absent in the case of application of ring out-of-plane deformation energy for quantitative estimation of aromaticity. Results of calculations demonstrate that aromatic ring in all molecules under consideration possesses a notable degree of conformational flexibility. Benzene is the most rigid molecule possessing the highest ring deformation energy. Presence of substituent results in an increase of aromatic ring flexibility and decrease of deformation energy. The lowest value of E_{def} is observed for the strongest substituents like amino, hydroxy, methoxy and nitro groups.

Comparison of values of different aromaticity indexes and Hammet constants of substituents reveals reasonable correlation between them. However, it should be noted that correlations foe electron donating and electron withdrawing substituents are different. In general electron-donating groups more actively perturb aromatic system.

1. T. M. Krygowski, K. Ejsmont, B. T. Stepien, M. K. Cyranski, J. Poater, M. Sola, J. Org. Chem., 69 (2004) 6634.
2. O. V. Shishkin, K. Yu. Pichugin, L. Gorb, J. Leszczynski, J. Mol. Struct. 616 (2002) 159.

Molecular structure and ring inversin of six-membered tetrahydroheterocycles

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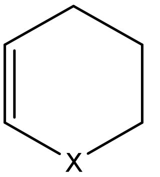
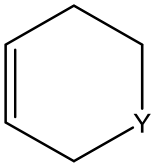
Recently [1] it was demonstrated that the ring inversion in cyclohexene includes three stages. The first stage is the transformation of the equilibrium half-chair conformation into a twist-boat conformation via the sofa conformation. This requires a significant increase in energy in the molecule. The second stage may be described as an extremely easy pseudorotation from one twist-boat form to another via boat. This process does not cause changein energy of molecule. The size of this plateau on the potential energy surface in terms of the value of the $C(sp^3)$-$C(sp^3)$-$C(sp^3)$-$C(sp^3)$ torsion angle is ±30° (DFT) and ±40° (MP2). Such characteristics in the energy profile results in the formation of a multitude of saddle points for the cyclohexene ring interconversion. From a physical viewpoint, almost all points within the plateau may be considered as saddle points. The third stage involves the transition from a twist-boat to a half-chair conformation accompanied by a significant decrease in energy.

The replacement one of the $C(sp^3)$ atoms in the molecule of the cyclohexene by the heteroatom (O, N, S, Se) leads to the conformation of the heterocycle becomes asymmetrical. One can assume that the loss of the symmetry will entail the essential changes of the conformational characteristics of the ring. Therefore, we performed the systematic investigation of the equilibrium geometry, ring interconversion barrier and a ring inversion pathway for the molecules **1-8** at the MP2/6-31G(d) level of theory.



1 X=O
2 X=NH
3 X=S
4 X=Se



5 Y=O
6 Y=NH
7 Y=S
8 Y=Se

Results of calculations demonstrate that the equilibrium conformation of the molecules **1-8** is an asymmetrical half-chair. The value of the barrier for ring inversion varies in widerange 2.14-7.74 kcal/mol depending on heteroatom. The most interesting results were obtained for ring inversion pathway. The potential energy profile for molecules **1-8** has lost three-stage character. This allows to determine unambiguously the conformation of the transition state. In the case of molecules **1, 2** and **5, 6** ring inversion profile has clear saddle point corresponding to boat conformation. However, the conformation boat is an additional minimum on the potential energy surface for the molecule containing the sulfur or selenium atom. Its energy is 2.23-5.90 kcal/mol higher as compared to equilibrium half-chair conformation. Accordingly two saddle points appear on the potential energy surface for these molecules. The conformation of the both transition states is a twist-boat. However, these saddle points have significantly different energy despite of similar conformation.

1. S.V.Shishkina, O.V.Shishkin, J.Leszczynski, Chem. Phys. Lett. 2002, v.354, №5-6, p. 428-434.

Ab initio modeling of K, Mg asparaginates in water solution

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The Potassium and Magnesium Asparahynates is substation for a preparation of Asparcam (Panangin) which is the mix of Potassium and Magnesium Asparahynates in ratio 1:1. Asparcam eliminates the electrolytic disbalance in the organism promoting the penetration of the potassium and magnesium iones into the intracellular space.

The information concerning structure and stability of K and Mg Asparahynates in the water solutions has paramount meaning for understanding of mechanisms of their carry through a cellular membrane.

To receive this information, the systematic theoretical study of atomic structure of various model compounds has been done. The charge distribution and bond characteristics (bond lengths and bond orders) were performed within the *ab initio* (Hartree-Fock, MINI) quantum-chemical methods. The Aspartic acid, Potassium Asparahynate + one molecule H_2O, Magnesium Asparahynates + fore molecules H_2O were considered for the calculations. After it super molecules K and Mg Asparahynates +20, 40 and 60 molecules H_2O have been calculated.

In all cases the structures were optimized by using the total energy minimization of the system. The structural formula of K and Mg Asparahynates +20 H_2O supermolecule after full geometry optimization is shown in Fig. 1.

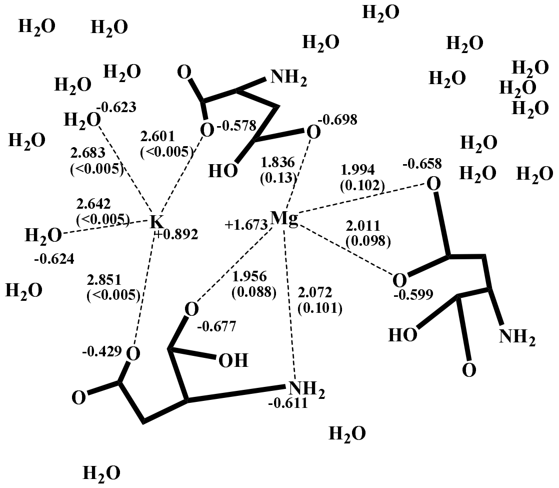

Fig.1. Structural formula of supermolecule, consist of $[AmCOO^-]_2 \cdot Mg^{2+}$, $[AmCOO^-] \cdot K^+$ and 20 molecules of H_2O, after *ab initio* calculation. In figure are shown charges on atoms in a.u., bond lengths in Å and bond orders (in brackets) in a.u.

Is was shown, that in the water solution K and Mg Asparahynates form the steady mixed complexes, the structural elements in which are connected by electrostatic interaction.

Hydrolysis with uranyl ion participation in water solution and adsorption of uranyl ion on SiO_2 surface

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The quantum chemical calculations (ab-initio method) are applied to investigate the formation of hydration shell of uranyl ion in water solutions. It is shown that the uranyl complex with five water molecules is the most stable one. The first and second stages of hydrolysis are investigated. The most stable is the complex with four water molecules and one hydroxyl (first stage) and the complex with three water molecules and two hydroxyls (second stage). The possibility of formation of polinuclear uranyl complex in water solutions is revealed. The charge distributions and distance between atoms in complexes are obtained. At the adsorption of uranyl ion in SiO_2 surface two cases are considered, the case when uranyl is adsorbed without hydration shell and the case when the presence of hydration shell is taking into account. The adsorption of the water molecules on the silicate surface is also investigated. The hydrolysis of water is present. The changes of the surface geometry, charge distribution, and adsorption energy is obtained.

SO(3)- invariant expansions for intermolecular interactions. Shape-factor on nanoscale under aspect of ordering in biological membranes and soft matters

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Expansions over rotational invariants are widely used in statistical mechanics of complex molecular systems [1-4]. They can be rendered into a computationally tractable form with an inherent structure perfectly suited for implementation on modern day computing architectures. Thus, it is possible to calculate numerous equilibrium observable properties, including both thermodynamic and structural quantities, in a computationally efficient manner. But not the last advantages of the methodology stem from the direct contact to analytical approaches. One can also note that expansion discussed is, in fact, a Fourier series (on group SO(3)). Just as in other applications of Fourier analysis in physics, it is not the sum of the series that is the most interesting, but its specific terms. From the mathematical point of view, one may say that purely physical effects are manifestations of playing these or those coefficients of corresponding Fourier series.

Our more recent investigations, however, focused on the development and study of the role of molecular shape in mesogenic systems and biological membranes. In this work, we propose a simple model of anisotropic IMI, accounting for real molecular structure considering first of all their long-range components.

For our problem, the most appropriate seem to be "standard" models of molecules used in computer modeling with real geometry, real values of atomic mass (hence, calculated moments of inertia), but with one difference. Namely: we assume that atoms of all molecules create similar force fields, i.e., the energy parameters characterizing atom-atom (non-valence) interactions are the same. Such a model reflect the ideas and perceptions of interaction of uniform ("homogeneous")molecules. As initial atom-atom potentials, we have chosen Lennard-Jones potentials (for non-valence interactions) and electrostatic. For model calculations, we chose typical mesogenic and model lipid molecules with various conformations.

With the view to understand numerous ordering phenomena in membranes, liquid crystals (and other soft matters), we have calculated the coefficients of SO(3)-invariant expansions, which characterize essential behaviour of the material under consideration, and their functional dependence from intermolecular distance. Basing on this results we discuss some theoretical problems of phase transition in membranes and liquid crystals and related distinct and common structural features.

1. Blum L., Torruella A.J. , *J.Chem.Phys*., **56**, 303 (1972) .
2. C.G.Gray, K.E.Gubbins. *Theory of molecular fluids.,* Oxford University Press, New York, 1984.
3. Shtifanyuk P. P., Shramkov A. N., Yakovenko S. E., Geiger A.,Physika A, Stat.theor.Phys., **195**, 398 (1993).
4. P.P.Shtifanyuk, A.V.Dyomin, L.N.Lisetski, S.E.Yakovenko **,** Functional Materials, **9**, 416 (2002).

Car-Parrinello molecular dynamic simulation of purine DNA bases in aqueous solution

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Ab Initio molecular dynamics simulations have been performed to minute study for purine DNA bases in explicit water environment. We present several theoretical models to investigate the structure and binding of adenine and guanine in aqueous solution. The first simulation model contains single adenine (guanine) within 54 water molecules network, using periodic boundary conditions. The model 2 represents bases in H_2O/H_3O^+ solvent environment with excess of hydronium ion, and the model 3 is the simulation of purine bases surrounded by H_2O/HO^- solvent. CPMD dynamics allowed us to observe both proton transfer from the H_2O/H_3O^+ solvent network to the specific site of guanine an adenine and typical deprotonation processes in presence of OH^- ion. These results open a new prospections for characterizing behavior of biologically important system at the molecular level.

One more important step forward has been made here by focusing on the excited-state protonated and unprotonated guanine and adenine in water solution. These results can lead to an improved understanding of the tautomeric transitions of DNA bases in water medium.

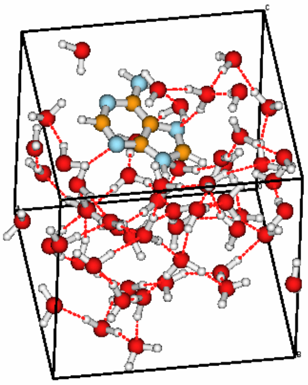

Fig. 1. Adenine within 54 water molecules network

We have provided direct insight into the motions of the first water shell with emphasis on the hydrogen bonds lifetime, mean number and configuration of water molecules (hydration number) in the first solvation shell. It has been shown that effect of hydrogen-bond cooperativity can differentiate the interactions between purines and waters and between water molecules.

In additionally radial distribution functions calculated from a Car-Parrinello molecular dynamics simulation of the aqueous solution clearly show an unusual hydrogen bonding of water to the nitrogen lone pairs of amino group and C-H group of guanine, as well as possibilities of water molecules to form simultaneously 2 hydrogen bonds to purines nitrogen atoms. Structure of solvent also has been discussed in the context of ab initio pair correlation functions.

Theoretical study of hydration and tautomer transitions of mono- and polyhydrates energetically low-lying tautomers of purine DNA bases

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In this work we investigate the structure and property of the water complexes of several energetically low-lying tautomers of adenine and guanine. Particularly emphasis was placed on geometry and energy of adenine monohydrates obtained from fully counterpoise corrected ab initio calculations at the MP2 and density functional theory level. We have found that transition barrier ($\Delta G^{\neq}$) oxo-hydroxy and amino-imino tautomer transitions for adenine and guanine monohydrates on PES corrected for BSSE remarkably differ (to 5 kcal/mol or 50%) from uncorrected values. Barriers of proton transfer reactions are found to be higher when counterpoise correction for PES was applied.

The energies and hydrogen bonds character in purine polyhydrates strongly depend on tautomeric form of bases and water network structure. Insignificant reorganization of water molecules results in change of Gibbs free energies up to 2 kcal/mol and more deep modification to 7-8 kcal/mol. The results show that hydration shell consisting of 12 water molecules dramatically stabilizes rare adenine tautomers but the solvation shell with 7 water molecules leads to destabilization (1-2kcal/mol) of polyhydrates in comparison with isolated systems. The stabilization by 7 kcal/mol due to hydration is typical of several of guanine tautomers. At the same time our calculations suggest that the hydroxy tautomers of guanine polyhydrates lose their stability (9 kcal/mol). The most populated resonance structure from NRT analysis (within Weinhold NBO Scheme) for canonical and rare tautomer forms and their contribution to geometry of complexes were also studied.

In addition ab-initio molecular dynamics simulations were carried out for both adenine monohydrates and complexes of guanine and adenine with 12 water molecules.

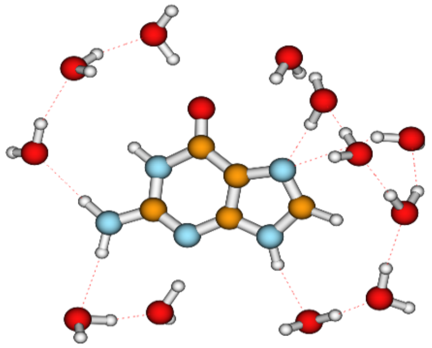

Fig. 1. Trajectory snapshot after 2.5 ps ab-initio MD simulation for Guanine-$12H_2O$ complex

Car-Parrinello molecular dynamics of Guanine-$12H_2O$ polyhydrate clearly show preference of water for hydrogen bonding to the guanine over the dissociation processes. Also MD reveals significant reorganization of hydration shell for adenine-$12H_2O$ complex. We find that the effect of hydrogen-bond cooperativity plays important role in polyhydrates.

Ab initio calculations of thermodynamics of the metathetical processes used for producing of the electrolytes for lithium batteries

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Lithium batteries are nowadays produced at high scale and used in various fields [1-3], that requires the development and introduction of new advanced methods of producing their components, particularly, stable electrolytes with high electric conductance. At present, solutions of fluoride complex salts, in first instance, lithium hexafluorophosphate, in the mixtures of carbonate esters with different polarity, are used most widely as electrolytes for rechargeable lithium-ion batteries. At the same time, traditional methods of the production of the electrolytes, consisting in preparing of thoroughly dried components following with obtaining of the solutions with desired concentration, are complicated by difficulties arising from high hygroscopicity and low thermal stability of lithium hexafluorophosphate.

We studied the possibility of producing of the electrolytes, consisting of lithium hexafluorophosphate solutions in the mixtures of carbonate esters, particularly, propylene carbonate (PC) and dimethyl carbonate (DMC), by carrying out metathetical reactions between potassium or sodium hexafluorophosphate and lithium tetrafluoroborate. The thermal stability of the fluoro complex salts used as starting materials is higher than that of $LiPF_6$. Ab initio calculations of the thermodynamics parameters of the discussed processes evidence about considerable influence of the nature of the reaction media and the size of the cation on both Gibbs energies and equilibrium conversions. The influences of the temperature and initial molar ratios of the reactants were investigated. It was found that that using of potassium salts allow to obtain the electrolytes of higher purity, than sodium ones, that is in agreement with the data on solubility of KBF_4 and $NaBF_4$ in the media investigated.

^{19}F and ^{31}P nuclear magnetic resonance spectroscopy and X-ray powder diffraction were used to check the results of the calculations as well as to identify of the products of reaction. The deviation between the data calculated by different methods and the experimental data is approximately 1 % for the potassium salt and a few percents for the sodium salt; and the general tendencies of the influence of the most important parameters on the discussed processes are not affected by the used methods [4].

1. A. Nazri, G. Pistoia. *Lithium Batteries: Science and Technology.* Kluwer Academic Publishers. **2004**, 708 p.
2. W. A. van Schalkwijk, B. Scrosati**.** *Advances in Lithium Ion Batteries.* Kluwer Academic / Plenum Publishers. **2002**, 513 p.
3. Brodd R. J., Tagava K. *Elektrokhim. Energetika (Electrochemical Power).* **2004**, *4*, 195.
4. A. V. Plakhotnyk, L. D. Tarasova, L. Ernst, R. Schmutzler. *Z. Anorg. Allg. Chem.* In press.

Quantum chemical simulation of oxidation processes on silicon surface within cluster approach

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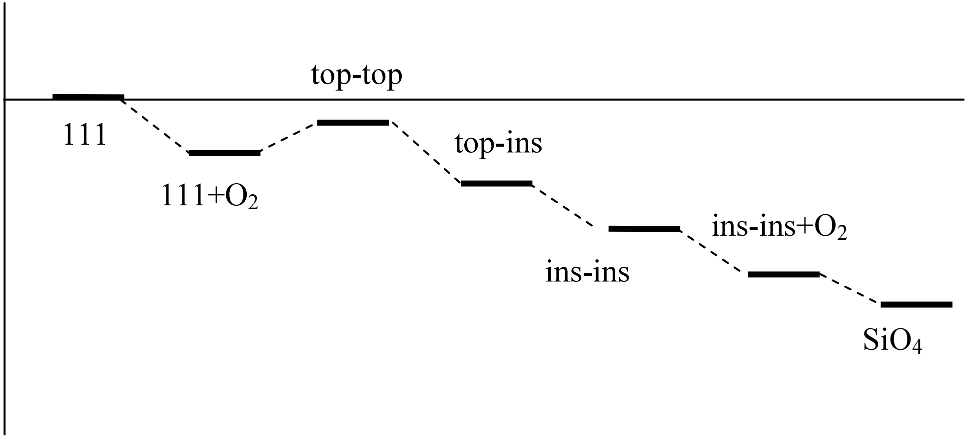
There are a lot of contradictions in the literature concerning the initial stages of oxidization of silicon surface and SiO_2 film formation. The properties of Si/SiO_2 critically affect work of the element base in microelectronics.

Taking into account a great role of collective interactions in silicon surface oxidation (well-known from literature data), in order to calculate the energies of SiO_2 layer formation, a cluster was built of $Si_{26}H_{24}$ with hydrogen atoms inserted at edge atoms for the saturation of "broken" bonds. The calculations were carried out by the density functional theory method.

A considerable degree of electronic density transfer from surface onto O_2 molecule is a characteristic of the supramolecular structure (chemisorbed oxygen molecule) formed on silicon face (111), which results in dissociative chemisorption with formation of Si-O groups at top position of neighboring silicon atoms. The energy of the cluster simulated for the structure of top-top is somewhat higher than that of the cluster which presents a chemisorbed complex of oxygen molecule on the face (111) of crystalline silicon. It means that the initial stage of the sequence of processes of SiO_2 formation needs a small activation energy. At a next stage one of atoms of oxygen is inserted into Si-Si bond between silicon atoms of surface and subsurface layers with formation of tor-ins structure. The further forming SiO_2 layer on the surface of crystalline silicon needs a formation of supramolecular chemisorption structure on the surface which already contains the two oxygen atoms intercalated into Si–Si bonds. Next transformation of the intermediate with participation of the second oxygen molecule is similar to the process of initial oxidation of crystalline silicon. As computations show the second oxygen molecule sits down on the silicon atom at which already has Si-O-Si bonds. Than oxygen atom is inserted into the Si–Si bond so completing SiO_4-tetraedron formation which is the only building block of silicon dioxide.

Thus, the complex of the results of computations fulfilled let it possible to elucidate the mechanism of formation of silica layer on the face (111) of crystalline silicon and to define the thermal effects of the separate stages of oxidation with molecular oxygen.



An energy profile of the consequent stages of silica film formation at (111) face of crystalline silicon. The energy zero level is believed to be the sum of total energies for the cluster(111) plus triplet state of oxygen molecule.

CASP validation of a novel protein homology modelling algorithm

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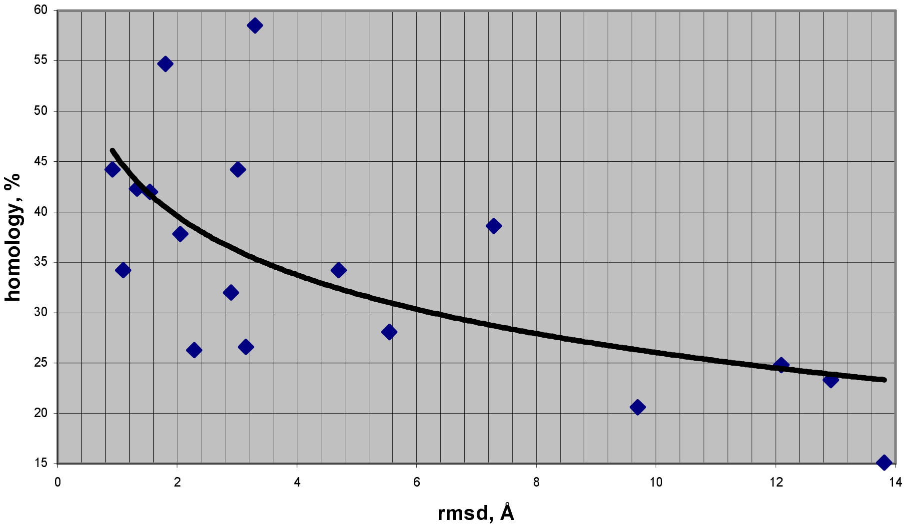
Prediction of protein three-dimensional structure from its sequence poses serious problem for computational biology. An approach called *homology modelling* allows structure prediction of proteins that have sequence homologues among proteins with known structures. It is based on an assumption that proteins with similar sequences will fold into similar structures. Homology modelling requires sequence alignment between *target* (protein to be predicted) and *template* (homologous protein used for prediction). This alignment must be done in such a way that the sequences of target aligned to the secondary structure elements (α-helices and β-strands) of the template are not interrupted by gaps. The 3D coordinates of the target backbone's α-helices and β-strands are copied from the atomic coordinates of the template backbone. The user may choose to copy loops of equal length or to model them *ab initio*. Loops, which connect secondary structure elements, are built *ab initio* using the downhill simplex minimization algorithm [1]. An energy function incorporating distance-dependent residue-residue potentials [2], validity of valent and dihedral angles formed between the last C-terminal loop residue and the first N-terminal secondary structure residue, and the distance between the last loop atom and the first secondary structure atom allows the loop to close and minimizes its energy at the same time [3]. The side-chains are placed using backbone-dependent χ-angles library [3].

Submission to CASP (<u>C</u>ritical <u>A</u>ssessment of <u>S</u>tructure <u>P</u>rediction) experiment is the best way to get independent validation of any new structure modelling algorithm [4]. We submitted four targets to CASP4 [3] and twenty-two to CASP5 [5]. In total, CASP assessors evaluated eighteen predictions. Several predictions were the best or among the best, compared to predictions submitted by other scientific groups. The graph below shows dependence of quality of our predictions (<u>r</u>oot <u>m</u>ean <u>s</u>quare <u>d</u>eviation from actual structure) versus percent of homology between target and selected template for all CASP targets submitted by us. This dependence allows rough estimation of prediction quality for unknown proteins.



1. Nelder, J. A., Mead, R. (1965) Computer J., 7:308-313.
2. Bahar, I., Jernigan, R.L. (1997) J. Mol. Biol., 266:195-214.
3. Tereshchenko, F.A., Daraselia, N.D. (2000) Proceedings of CASP4 Conference, 50-51.
4. http://predictioncenter.llnl.gov
5. Tereshchenko, F.A. (2002) Proceedings of CASP5 Conference, 87-88.

On the problem of the interaction mechanism of silica nanoparticles with plasmatic membrane

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Quantum chemistry has achieved a level, which let it possible to research not only the structures of isolated small molecules, but also those of separate fragments of biological molecules as well as the mechanism and energetics of their interaction between each other and with solvent molecules. An addition, development of new organic-inorganic drugs puts forward a problem of justifying the detailed mechanism of the interaction of chemically active solid surface with the elements of physiological media of living bodies. First of all blood cells – erythrocytes – belong to them.

In this study a method has been proposed of calculation of the energy and mechanism of the interaction between the clusters simulated for hydroxylated silica nanoparticle with negative surface charge and lipid area of negative charged surface of plasmatic membrane. As both interacting species have the same sign of charge and the experiment gives an evidence of their cohesion, in order to provide converging clusters, we propose to put mono- and dihydrated protons between these clusters. If the total charge of this supramolecular structure is believed to be zero, an optimization of spatial parameters results in the formation of a water-bonded complex.

Thus, we can jump to the conclusion that accordingly to the results of calculations, the interaction between silica nanoparticles and plasmatic membrane at large distances (5 to 7 Å) is provided with charged electrolyte particles whereas at the distances where the orbital overlap of edge atoms is essential, a net is formed of hydrogen bonds.

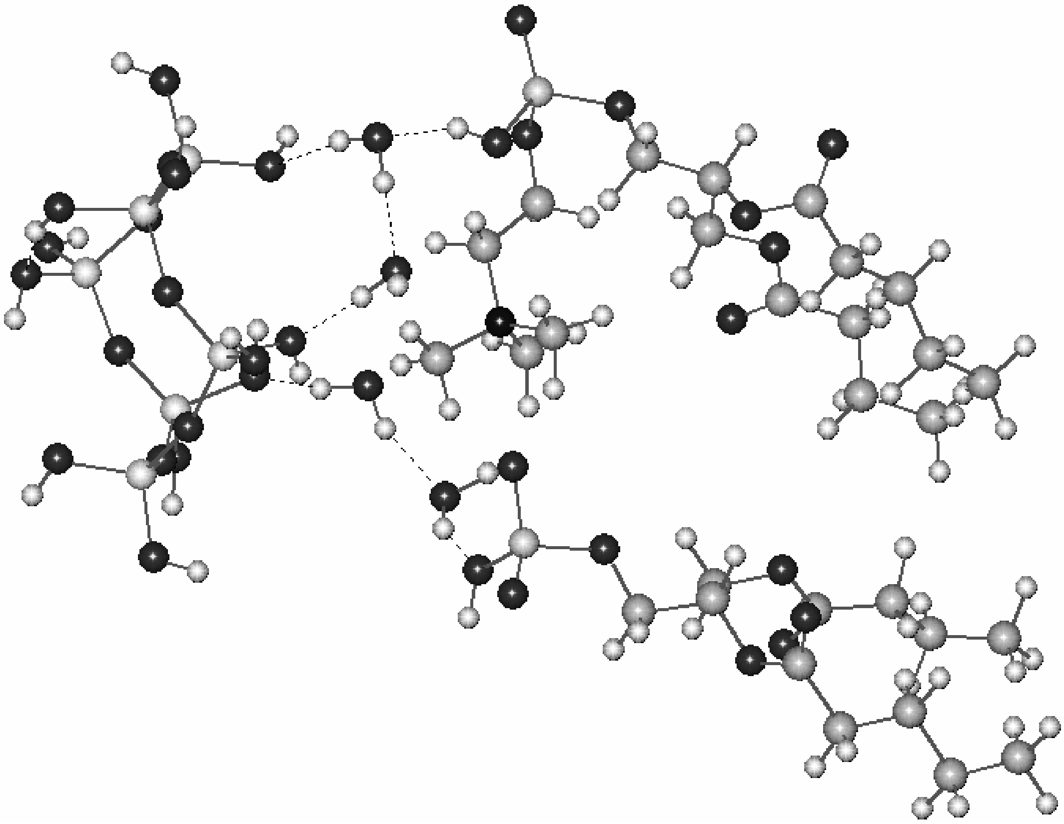

Fig. Equilibrium spatial structure of the complex where water molecule provide binding between a fragment of SiO_2 surface and lipid area of plasmatic membrane

Quantum chemical modelling of homolytic decomposition reactions of arylalkyl hydroperoxides

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To estimate structure effects of arylalkyl hydroperoxides upon their reactivity the molecular modelling of peroxide bond homolysis reaction of the isopropylbenzene hydroperoxide (ROOH), 1,1-dimethyl-3-phenylpropyl hydroperoxide (R_1OOH), 1,1-dimethyl-3-phenylbutyl hydroperoxide (R_2OOH), and 1,1,3-trimethyl-3-(*p*-methyl)-phenyl (R_3OOH) hydroperoxide was carried out. Equilibrium hydroperoxides configurations used in all quantum chemical calculations were obtained by semiempirical AM1 method in RHF approximation realized in MOPAC-97 package.

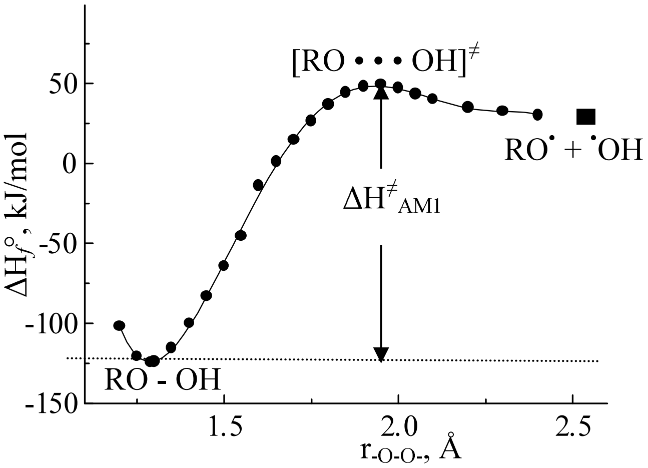

Fig. 1. The minimum energy path of R1OOH homolytic decomposition reaction

All investigated hydroperoxide compounds have the same configuration of the hydroperoxide fragment (-COOH) which is scarcely depends upon hydroperoxide molecule structure. Calculation of the minimum energy reaction path of peroxide bond cleavage was carried out with accounts of electron correlation. It is a smooth curve (Fig. 1) which passes through a maximum and comes to the stationary value corresponding to the sum of two radicals energy (the such curve is typical for the endothermic reactions). Transition state of the system was localized by elongation of peroxide bond from 1.29 to 1.95 Å.

For the hydroperoxides under investigation the value of transition state formation enthalpy is lineary depended upon the value of hydroperoxide formation enthalpy in the ground state. The relationship obtained will allow estimating of homolysis activation enthalpy for another hydroperoxides of present series and also the number of configurations nessesary for the electron correlation accounting.

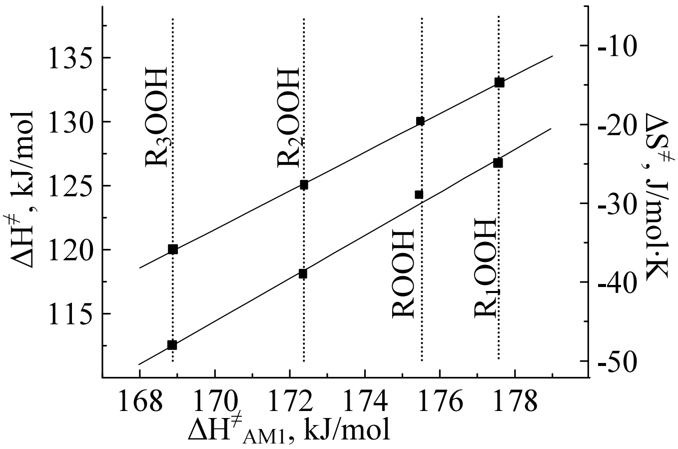

Fig. 2. Relationship between experimental activation parameters of the arylalkyl hydroperoxides decomposition and the calculated activation enthalpy of their homolysis

Activation enthalpy values estimated by quantumchemical methods are linearly depended upon experimentally obtained activation parameters of arylalkyl hydroperoxides thermolysis in acetonitrile (Fig. 2). Thus obtained relationships allow to estimate the kinetic parameters of thermal decomposition reactions of the arylalkyl hydroperoxides on the base of quantum-chemical modeling of the peroxides bond homolysis for the present compounds series.

The computational modelling of the monolayer adsorption isotherms in disordered media

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One of the effective methods of the monolayer adsorption isotherms description in non-ordered media is the method of integral equations. For this method application one should know *a priori* the adsorption centres distribution function which is difficult to choose due to the lack of reliable thermodynamic criteria. Besides the known integral equations solutions are as a rule non analytical ones. This work suggests application of the fractional integral equations for adsorption isotherms description in the non-ordered media.

The function

$$(I_0^{\alpha} f)(x) = \frac{1}{\Gamma(\alpha)} \int_0^x (x-t)^{\alpha-1} f(t)dt, x > 0$$

is called left-side integral of Riemann-Liouville of order $\alpha > 0$ for function $f(x) \in L(0,c)$, where $\Gamma(\alpha)$ is Gamma function. Let $\alpha \in (0,1)$ and $f_{1-\alpha}(x) = (I_0^{1-\alpha} f)(x)$.

If function $f_{1-\alpha}(x)$ almost everywhere on $(0,c)$ has a derivative, then function $(D_0^{\alpha} f)(x) = f'_{1-\alpha}(x)$ is called left-side derivative of Riemann-Liouville of order $\alpha > 0$.

Let values (x_i, Y_i) be obtained from the experiment. We'll talk about approaching mathematical model of the next task:

$$(D_0^{\alpha} y)(x) = ay(x) + b, y_{1-\alpha}(0) = 0. \tag{1}$$

We will look for solution of task (1) in the class of continuous on $[0,c]$ functions. Function $y(x)$ is the solution of task (1) if and only if it is the solution of integral equation

$$y(x) = \frac{bx^{\alpha}}{\Gamma(\alpha+1)} + \frac{a}{\Gamma(\alpha)} \int_0^x (x-t)^{-\alpha} y(t)dt. \tag{2}$$

Solution of equation (2) has a view

$$y(x) = \frac{b}{a}(E_{\alpha}(ax^{\alpha}) - 1),$$

where $E_{\alpha}(z) = \sum_{k=0}^{\infty} \frac{z^k}{\Gamma(\alpha k+1)}$ is the Mittag-Leffer function.

If $y_k \approx y(x_k)$, then $y_0 = 0$, $y_1 = \frac{bx_1^{\alpha}}{\Gamma(\alpha+1)}$, and

$$y_k = \frac{bx_k^{\alpha}}{\Gamma(\alpha+1)} + \mathrm{a} \sum_{i=1}^{k-1} y_i((x_k - x_i)^{\alpha} - (x_k - x_{i+1})^{\alpha}), \quad k \geq 2. \tag{3}$$

Values of parameters a, b, α can be found as minimum of functional

$$\Phi(\alpha, \mathrm{a}, b) = \sum_{k=0}^{N} (y_k - Y_k)^2.$$

If the mentioned above variables are given the physical sense of the adsorptional system defining parameters - the monolayer capacity ($y = \theta$), the Henry constant (b) and the disorderliness parameter (α), it is possible to carry out the computer modelling of the monolayer adsorption isotherm in disordered media by means of Equation (3).

Application of methods of computation chemistry for investigation of geometries and ^{1}H and ^{13}C NMR spectra of 1-vinylimidazole and 1-vinyl-2-methylimidazole

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Ab initio calculations of geometries for molecules of 1-vinylimidazole (**1**) and 1-vinyl-2-methylimidazole (**2**) were carried out by Gaussian 98W program package with different basis sets (6-31G, 6-311(d,p)) and different methods: HF and B3LYP. The molecular energy potential of compounds (**1**) and (**2**) as a function of the rotational angle around bond N(1)-C(alpha) were obtained.

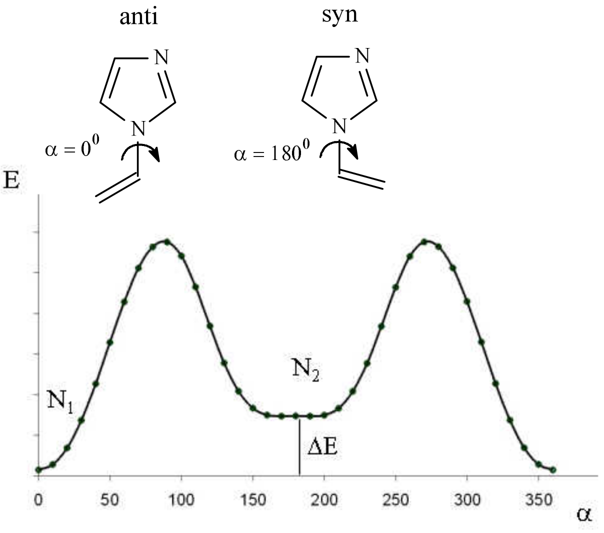

Fig. 1

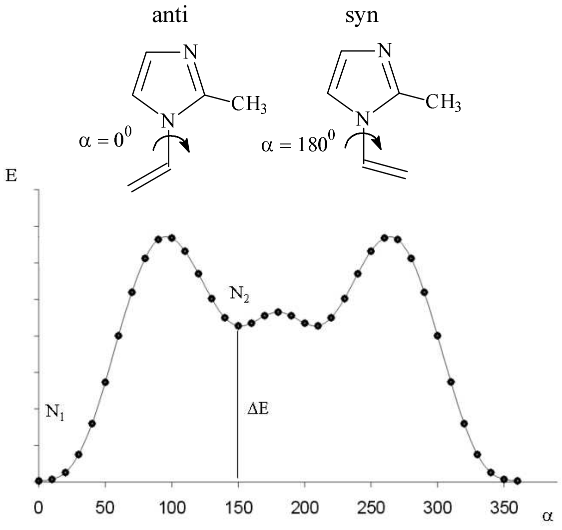

Fig. 2

Two minima are located on the potential energy surface of compounds (**1**) corresponding to planar conformers with different spatial orientation of vinyl group: anti-C(2) (global minimum) and sin-C(2) (local minimum) (Fig. 1). The energy difference ΔE is estimated as 0.48 - 0.84 Kcal/mol according to different methods. Partial populations N_1, N_2 for two conformers were evaluated as 0.8 (anti-) / 0.2 (syn-) from Boltzmann equation for relative population.

Three minima are located on the potential energy surface of compounds (**2**) corresponding to planar conformer with anti-arrangement vinyl group and 2-methyl group (global minimum) and two symmetrical minima (local minima) corresponding non-planar sin-orientation of vinyl group and 2-methyl group (Fig. 2). Two local minima correspond to the torsion angle 30 degree complying to the location of vinyl group out of plane imidazole ring. The energy difference ΔE amounts 2.06 to 1.6 Kcal/mol according to different methods. Partial populations N_1, N_2 for tree conformers were evaluated as 0.97 (anti) / 0.03 (syn).

^{1}H and ^{13}C NMR shielding constants were computed via GIAO method for conformations corresponding to the states in global and local minima of energy. The value of chemical shifts were averaged by partial populations. The best correspondence with experimental data were achieved on method B3LYP with basis set 6-31G.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 03-03-32310).

A priori information and constructing of regularizing algorithms for calculation of molecular force fields

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Many problems of science, technology and engineering are posed in the form of operator equation of the first kind with operator and right part approximately known. Often such problems turn out to be ill posed. It means that they may have no solutions, or may have non-unique solution, or/and these solutions may be unstable. Usually, non-existence and non-uniqueness can be overcome by searching some "generalized" solutions, the last is left to be unstable. So for solving such problems is necessary to use the special methods - regularizing algorithms.

The theory of solving linear and nonlinear ill-posed problems is advanced greatly today (see for example [1, 2]). A general scheme for constructing regularizing algorithms on the base of Tikhonov variational approach is considered in [2].

It is very well known that ill-posed problems have unpleasant properties even in the cases when there are existed stable methods (regularizing algorithms) of their solution. So at first it is recommended to study all a priori information, to find all physical constraints, which may make it possible to construct a well-posed mathematical model of the physical phenomena.

Computational programs for linear ill-posed problems with a priori information (monotonicity, convexity, known number of extremes, sourcewise representation of unknown solution, etc.) could be found in [1] and generalized for nonlinear problems also. If the constraints are not sufficient to make a problem well posed, then it is necessary to use all these constraints but we must also know error level of experimental data. As example of successful applications of these regularizing algorithms to practical problems we consider inverse problems of vibrational spectroscopy [3]. For overcoming the ill-posedness of inverse vibrational problem we've proposed to use the quantum mechanical data as an additional information and as a stabilizer within the regularization procedure while looking for the Regularized Quantum Mechanical Force Field (RQMFF) [3]. New enlarged physical model for the determining the force field parameters within regularizing algorithms are proposed which consider the large amplitude motion and anharmonicity effects. Quantum mechanical data also serve as a priori information on molecular force field model.

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1. A.N. Tikhonov, A.V. Goncharsky, V.V. Stepanov, and A.G. Yagola, Numerical methods for the solution of ill-posed-problems: Kluwer Academic Press, Dordrecht, Netherlands (1995).
2. A.N. Tikhonov, A.S. Leonov, and A.G. Yagola, Nonlinear ill-posed problems, vol. 1, 2: Chapman and Hall, London, England (1995).
3. A.G.Yagola, I. V. Kochikov, G.M.Kuramshina, Yu.A.Pentin, Inverse Problems of Vibrational Spectroscopy, VSP, Zeist, The Netherlands, (1999).

Favorable silica monolayer structures on the Mo(112) surface

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Favored structures of SiO_n monolayers on the Mo(112) surface have been studied using the total energy minimization technique (as implemented in the FHI98md code) based on DFT semirelativistic approach. In the $[SiO_4]$ complexes, which form the c(2×2) silica structure on the Mo(112), the bonding of the Si atoms with the surface is accomplished through the oxygen atoms. The structure with a symmetric position of oxygen atoms has been found to be the most favorable. In this structure, two oxygen atoms occupy bridge-on-row sites on the Mo(112) surface, with Si atoms between them, while oxygen atoms in the troughs appear not in expected threefold sites, but adjust their positions along the middle lines of the troughs. Estimated main phonon frequency and density of states for the symmetric $[SiO_4]$ structure agree well with experimental results.

Comprehensive conformational analysis of 1'-deoxyribose, model sugar motif of ribonucleosides. DFT quantum chemical investigation

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We have firstly applied comprehensive conformational analysis of 1′ -deoxyribose, model sugar motif of isolated ribonucleosides, using NWChem code at the MP2/6-11++G(d,p)//B3LYP/6-31G(d,p) level of theory.

We analysed geometric and electronic structure of all conformers. The emphasis was underlined to the most energy optimal ones. It should be noted that C2′- endo and C3′- endo conformational families are the most populated.

The intermolecular OH…O H-bonds were analysed in all found conformations. These H-bonds have been identified by means of geometric and spectral criteria. Furthermore, we applied topological descriptions of the electronic density. As a result, AIM criteria were crucial in H-bonds determination in the majority of cases.

The biophysical importance of the obtained results is discussed, first of all their application in isolated ribonucleosides' conformational analysis.

Alternative wave–function ansätze in the state-specific multireference coupled cluster theory

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The coupled cluster (CC) theory is one of most exact quantum chemistry method for describing the ground state of molecule. While the CC procedure for calculating the ground electronic state is well established, a similar procedure for the calculation of electronic excited and quasi degenerate states is still lacking. The absence of a routine CC approach to excited states can be attributed to the problem with developing a "natural" CC ansatz for such cases. In general, one would like to write the CC wave function for the ground state or an excited state in the following simple form:

$$|\Psi_{\mathrm{CC}}\rangle = \mathrm{e}^{\hat{\mathrm{T}}}|0\rangle. \tag{1}$$

While for the closed–shell ground state the Hartree–Fock determinant ($|0\rangle$) is the obvious choice for the reference wave function, for open shell states the reference wave function has to include in most cases several determinants that provide an adequate first–order description of the considered state. In our recent works for excited and quasi–degenerate states we have considered and tested in the calculations some new approaches. Among those the one that can handle the general quasidegeneracy problem is based on the following (semi–linear, SL) form of the CC wave function:

$$|\Psi_{\mathrm{SLCC}}\rangle = \mathrm{e}^{\hat{\mathrm{T}}^{(\mathrm{ext})}}(1 + \hat{\mathrm{C}}^{(\mathrm{int})})|0\rangle. \tag{2}$$

In this wave function the *internal* operator $\hat{\mathrm{C}}^{(\mathrm{int})}$ by acting on the formal reference ($|0\rangle$) generates the model–space reference function, while the external operator $\mathrm{e}^{\hat{\mathrm{T}}^{(\mathrm{ext})}}$ generates excitations outside the model space. The SL CC approach has been implemented as complete active space CCSD method (CAS(n,m)CCSD). The CAS(n,m)CCSD wave function has the following form:

$$|\Psi_{\mathrm{CAS(n,m)CCSD}}\rangle = \mathrm{e}^{\hat{\mathrm{T}}_1^{(\mathrm{ext})}+\hat{\mathrm{T}}_2^{(\mathrm{ext})}}(1 + \hat{\mathrm{C}}^{(\mathrm{int})})|0\rangle, \tag{3}$$

where $\mathrm{e}^{\hat{\mathrm{T}}^{(\mathrm{ext})}}$ generates all single and double electron excitations from *all reference functions* which arise by distribution of n electrons among m spin–orbitals. The $(1+\hat{C}^{(\mathrm{int})})|0\rangle$ is the CAS(n,m) wave function. The CC method based on (3) can be also applied to calculate excited states (CASCCSDx). For an excited state dominated by a one–electron excitation from the Hartree–Fock determinant, the reference space is generated by using unitary excitation operators $\hat{E}_{AI}$, which represents electron promotion from an occupied orbital (I) to an unoccupied orbital (A). In this case the CASCCSDx wave function can be written as:

$$|\Psi_{\mathrm{CASCCSDx}}\rangle = \mathrm{e}^{\hat{\mathrm{T}}^{(\mathrm{ext})}}\hat{\mathrm{E}}_{\mathrm{AI}}|0\rangle. \tag{4}$$

The wave functions (1–4) involve explicit inclusion of some high–order (more than two–electron) excitations from the formal reference determinant. An alternative to such approach is *nonexplicit* accounting for the higher k-order excitations. That alternative approach involves including additional projections in the CC amplitude equations. The resulting terms have the following form:

$$\mathrm{S_k}\begin{pmatrix} a_1\, a_2\, \dots\, a_k \\ i_1\, i_2\, \dots\, i_k \end{pmatrix} = \langle {}^{a_1\, a_2 \dots a_k}_{i_1\, i_2 \dots i_k}|\hat{\mathrm{H}} - \mathrm{E_{CC}}|\mathrm{e}^{\hat{\mathrm{T}}_2}\mathrm{CAS}\rangle, \tag{5}$$

The CC method with additional terms representing higher excitations in the amplitude CC equations has been tested on some model systems and the results are encouraging.

Tautomeric transformations of nucleotide bases in model systems of protein-nucleic acid recognition. Quantum chemical and experimental data

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Tautomerism is one of the most intriguing features of nucleic acid bases. Dozens of publications (mainly theoretical) were devoted to this subject. We came across this problem in the course of spectroscopic investigations of elementary of protein–nucleic acid recognition *via* carboxylic group of amino acids.

In some cases, interpretation of UV, IR and ^{1}H NMR spectroscopic data was impossible without suggestion of tautomeric transformatoins of the bases in their complexes in DMSO with deprotonated carboxylic group of amino acids modelled by sodium acetate ($CH_3COO^-Na^+$).

Quantum chemical calculations of Ade, isoGua, Pur and Xan tautomers' complexes with carboxylate ion of acetic acid CH_3COO^- , for the first time performed at our Department, gave evidence of transitions of the bases from ground-state to tautomeric forms to high-energy ones:
AdeN9H→AdeN7H, isoGuaN9H→isoGuaN7H, PurN9H→PurN7H and XanN7H→XanN9H which agrees with experimental data.

Vanishing of the imino proton signals of Ura and Thy in their ^{1}H NMR spectra in DMSO in the presence of sodium acetate gave rise to the idea that enolic forms of the bases are involved into the complex formation.

The MP2/6-31G(d,p)//HF/6-31G(d,p) calculations of complexes of Ura tautomers of the CH_3COO^-: Ura type does not explain vanishing of both imino proton signals:

In the course of spectroscopic investigations of elementary processes of protein-nucleic acid recognition *via* carboxylic group of amino acids there arose the problem of nucleotide bases' tautomerism. In some cases, interpretation of UV, IR and ^{1}H NMR spectroscopic data was impossible without suggestion of tautomeric transformatoins of the bases in their complexes in DMSO with deprotonated carboxylic group amino acids modelled by sodium acetate.

Quantum chemical calculations of energies of Ade, isoGua and Xan tautomer complexes with CH3COO$^-$ gave evidence of transitions from ground-state tautomers to high-energy ones: AdeN9H→AdeN7H, isoGuaN9H→isoGuaN7H and XanN7H→XanN9H, which agrees with experimental data.

In the case of Ura results of the MP2/6-31G(d,p)//HF/6-31G(d,p) calculations of its tautomer complexes of the CH3COO$^-$:Ura type did not explain vanishing of both imino proton signals in ^{1}H NMR spectrum. Only taking into account an impact of Na$^+$ in the triple complexes of the CH3COO$^-$:Ura:Na$^+$ type, it was shown that both enolic tautomers of Ura proved to form much more stable complexes (with slight energy gap between them) than the ground-state diketo one. Coexistence of two enolic tautomers fits experimental results.

The B3LYP/6-311++G(d,p) calculations of similar triple complexes of Ade tautomers showed that, except the ground-state complex of high-energy tautomer AdeN7H, two more high-energy tautomers (imino-AdeN3H,N9H and AdeN1H) form complexes more stable than the ground-state tautomer AdeN9H. According to calculations at the same level of theory, in the ground-state triple complex m^{9}Gua exists as the ground-state tautomer m^{9}GuaN1H, but energy of high-energy tautomer m^{9}GuaN3H in triple complex is 8 times reduced as compared to isolated state.

Every triple complex of all the bases' tautomers studied is stabilized by two H-bonds with CH3COO$^-$ and the most favourite coordinations with Na$^+$. In all the cases theoretical data completely agree with conclusions extracted from spectroscopic studies.

Thus, for the first time tautomeric transformations of nucleic acid bases in model systems of protein-nucleic acid recognition were detected, role of Na$^+$ in such processes being elucidated. Biological significance of high-energy tautomers of nucleotide bases is emphasized.