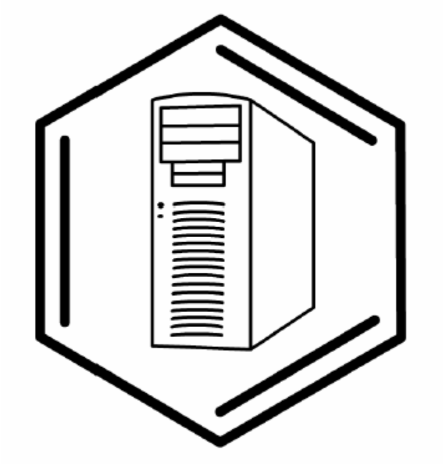
STC "INSTITUTE FOR SINGLE CRYSTALS" NAS OF UKRAINE
INSTITUTE OF MOLECULAR BIOLOGY AND GENETICS NAS OF UKRAINE
COMPUTATIONAL CENTER OF MOLECULAR STRUCTURE AND INTERACTIONS, JACKSON STATE UNIVERSITY, USA
TECHNOLOGY PARK "INSTITUTE FOR SINGLE CRYSTALS"
UKRAINIAN-AMERICAN LABORATORY OF COMPUTATIONAL CHEMISTRY



BOOK OF ABSTRACTS

Methods and Applications of Computational Chemistry

•

2ND INTERNATIONAL SYMPOSIUM

Kyiv, Ukraine, 2 - 4 July 2007

Kyiv - Kharkiv 2007

Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE **04 JUL 2007**	2. REPORT TYPE	3. DATES COVERED **00-00-2007 to 00-00-2007**

4. TITLE AND SUBTITLE **Book of Abstracts Methods and Applications of Computational Chemistry**	5a. CONTRACT NUMBER 5b. GRANT NUMBER 5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S)	5d. PROJECT NUMBER 5e. TASK NUMBER 5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **SSI Institute for Single Crystals,Lenin ave., 60,61077, Kharkiv-77, Ukraine,**	8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) **U.S. Army Corps of Engineers, Engineer Research and Development Center (ERDC-IRO), International Research Office**	10. SPONSOR/MONITOR’S ACRONYM(S) 11. SPONSOR/MONITOR’S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution unlimited

13. SUPPLEMENTARY NOTES

2nd International Symposium on Methods and Applications of Computational Chemistry, 2-4 July 2007, Kyiv, Ukraine

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**	**Same as Report (SAR)**	**106**	

Methods and Applications of Computational Chemistry

2nd International Symposium

Under support of International Research Office of the U.S. Army Engineer Research and Development Center (ERDC-IRO)

International Organizing Committee

Jerzy Leszczynski (Chairman), *Jackson State University, USA*
Ganna Elska (Honorary Chairman), *Institute for Molecular Biology and Genetics, Ukraine*
Volodymyr Seminozhenko (Honorary Chairman), *STC "Institute for Single Crystals", Ukraine*
Mikhail Bazilevsky, *Karpov Institute of Physical Chemistry, Russia*
Leonid Gorb, *Jackson State University, USA, and Institute of Molecular Biology and Genetics, Ukraine*
Jiande Gu, *Shanghai Institute of Materia Medica, China*
Dmytro Hovorun, *Institute of Molecular Biology and Genetics, Ukraine*
Ilya Kaplan, *National Autonomous University of Mexico, Mexico*
Jacek Karwowski, *Nicolaus Copernicus University, Poland*
Zdzislaw Latajka, *University of Wroclaw, Poland*
Manuel Ruiz-López, *Henry Poincare University, France*
Oleg Shishkin, *STC "Institute for Single Crystals", Ukraine*
Andrzej Sokalski, *Wroclaw University of Technology, Poland*
Jiří Šponer, *Institute of Biophysics, Czech Republic*
Miquel Solà, *Universitat de Girona, Spain*

Local Organizing Committee

Oleg Shishkin (Chairman), *STC "Institute for Single Crystals", Ukraine*
Dmytro Hovorun (Co-Chairman), *Institute for Molecular Biology and Genetics, Ukraine*
Leonid Gorb, *Jackson State University, USA, and Institute of Molecular Biology and Genetics, Ukraine*
Iryna Kolomietz, *Institute for Molecular Biology and Genetics, Ukraine*
Olha Korzh, *Institute for Molecular Biology and Genetics, Ukraine*
Yanina Mishchuk, *Institute for Molecular Biology and Genetics, Ukraine*
Svitlana Samijlenko, *Institute for Molecular Biology and Genetics, Ukraine*
Yuriy Varseev, *STC "Institute for Single Crystals", Ukraine*
Oleg Zhikol, *STC "Institute for Single Crystals", Ukraine*

Principal impossibility of the developed DFT approaches to describe the spin and space degenerate states

Ilya G. Kaplan

Instituto de Investigaciones en Materiales, Universidad Nacional Autónomo de México, Apdo. Postal 70-360, 04510 México, D.F. México; E-mail: kaplan@iim.unam.mx

The problems in the density functional theory arising when it is applied to the spin- and space-degenerate states are discussed. It is rigorously proved that in the case of orthonormal orbital set, the electron density of an arbitrary N-electron system does not depend upon the total spin S and for all values of S has the same form as it has for a single-determinantal wave function [1]. From this follows that the conventional Kohn-Sham equations, cannot distinguish the states with different total spin values.

A critical survey of the existing DFT methods of taking into account the total spin is performed. It is shown that all these methods, including state- and orbital-dependent functional method, modify only the expression for the exchange energy and use, if use, the correlation functionals not corresponding to the total spin of the state. It is also proved that the diagonal element of the density matrix is invariant with respect to the symmetry of the state, hence in the density matrix description there is no difference between degenerate and nondegenerate states. On the other hand, for the degenerate states the Born-Oppenheimer approximation fails that make impossible to apply the density functional formalism.

[1] I.G. Kaplan, *J. Mol. Struct.* (in Press), available online:
http://dx.doi.org/10.1016/j.molstruc.2007.01.012

Significance and applications of local ionization energies

Peter Politzer

Department of Chemistry, University of New Orleans, New Orleans, LA 70148, USA

The local ionization energy $\overline{I}(\mathbf{r})$, defined originally within the framework of Hartree-Fock theory but equally applicable in terms of Kohn-Sham density functional methods, is a measure of the energy needed to remove an electron at any point **r** in the space of a system. The focus is upon the particular point rather than upon a specific orbital. $\overline{I}(\mathbf{r})$ has been shown to be related to atomic shell structure, local kinetic energy (or temperature), atomic electronegativity and local polarizability. It can also be used as a means for identifying the radical characters of molecular sites as well as predicting and ranking their susceptibilities to electrophilic attack. An overview of these various aspects of $\overline{I}(\mathbf{r})$ will be presented.

Exponential Type Orbital Package: strategy and applications for NMR

Philip E. Hoggan

LASMEA, UMR 6602 CNRS.
University Blaise Pascal, 24 avenue des Landais, 63177 AUBIERE Cedex, France

This work uses exponential type functions (ETFs) as a basis set satisfying the nuclear cusp condition. The choice of Coulomb Sturmian basis functions is motivated by the fact that they constitute a complete set without continuum states. They also orthogonalise the Coulomb attraction [1].

The code structure is modular with many pre-calculated coefficients stored and retrieved from look-up tables. This includes Gaunt coefficients, optimal exponents, normalization constants and atomic integrals [2-3].

Efficient orbital rotation techniques are implemented to facilitate the use of a DIM (Diatomics in Molecules) strategy [4-5].

Finally, applications to precise evaluation of NMR chemical shifts are given to illustrate why Sturmians are far superior to Slater type orbitals in this case [6].

[1] C. A. Weatherford, E. Red and P. E. Hoggan, *Mol. Phys.* **103** (2005) 2169 and references therein.
[2] D. Pinchon and P. E. Hoggan, *Int. J. Quantum Chem* **107** (2007) online.
[3] J. Avery, *Hypersperical harmonics and generalized Sturmians*, Kluwer, Dordrecht. 2000.
[4] D. Pinchon and P. E. Hoggan, *J. Phys.* A. **40** (2007) 1597-1610.
[5] N. Absi and P. E. Hoggan, *Int. J. Quantum Chem* **106** (2006) 2881-2888.
[6] P. E. Hoggan, *Int. J. Quantum Chem* **100** (2004) 214-220.

Quasi-exactly solvable models of atoms and molecules

Jacek Karwowski

Instytut Fizyki, Uniwersytet Mikołaja Kopernika, Grudziądzka 5, PL-87-100 Toruń, Poland

The Schrödinger equation for two unconfined interacting particles may always be reduced to a system of two one-particle equations: One for the relative motion of the particles and another one for the motion of the centre of mass. Among textbook examples the best known are the hydrogen atom and the nuclear motion in the diatomic molecule. In general, this separation is impossible if the motion of the particles is confined by an external potential (e.g. two interacting electrons confined by a Coulomb potential modelling a helium-like atom). The only confinement which does not obstruct the separability is the one by a parabolic potential. The resulting system is known as the *Hookean atom* or *harmonium*. The analytical solutions to the problem were for the first time found by Santos [1]. Then the system was rediscovered several times (see e.g. [2]). A detailed analysis of its spectrum and studies on some related systems may be found in ref. [3]. Two simple properties of quadratic forms: (1) A linear combination of quadratic forms is a quadratic form, and (2) A linear transformation of the variables transforms a positive definite quadratic form to the diagonal form with positive coefficients, imply that also a Hookean molecule can be reduced to a similar, exactly-solvable problem. Recently constructed exactly solvable models of molecules [4] offer a possibility of a precise analysis of the Born-Oppenheimer approximation.

The problem is more difficult in the case of relativistic systems. However several examples of exactly and quasi-exactly solvable models described by either Dirac or Klein-Gordon equation have recently been discussed [5].

One can construct many exactly and quasi-exactly solvable one-particle Schrödinger equations with potentials appropriate to modelling systems relevant for quantum chemistry. Methods appropriate for the construction of such equations will be discussed and new approaches to the problem will be proposed. In particular, we are going to show some relations between the interaction potential and the form of the ansatz function which leads to the analytical solutions. In this way, a large class of exactly solvable problems may be obtained. Besides, we show how the recursive procedure of determining the form of the wavefunction may be transformed to an eigenvalue problem of a symmetric matrix. At the end, we shall discuss usefulness of some less common techniques as, for example, the ones based on the triconfluent Heun equation.

[1] Santos E. Calculo aproximado de la energia de correlacion entre dos electrones // *An R Soc Esp Fis Quim* **64** (1968) 177-193

[2] Taut M. Two electrons in an external oscillator potential: Particular analytic solutions of a Coulomb correlation problem // *Phys Rev* A**48** (1993) 3561-3566

[3] J. Karwowski and L. Cyrnek, Two interacting particles in a parabolic well: Harmonium and related systems // *Comp. Methods Sci. Technol.* **9** (2003) 67-78; Harmonium // *Ann. Phys.* (Leipzig) **13** (2004) 181-193; A class of exactly-solvable Schrödinger equations // *Collect. Czech. Chem. Commun.* **70** (2005) 864-880.

[4] X. Lopez, J. M. Ugalde, L. Echevarría, E. V. Ludeña, Exact non-Born-Oppenheimer wave functions for three-particle Hookean systems with arbitrary masses, *Phys Rev* A**74** (2006) 042504.

[5] M. Stanke, J, Karwowski and H. Tatewaki, Kinetically Balanced Dirac Equation: Properties and applications // *Mol. Phys.* **104** (2006) 2085-2092; J. Karwowski and G. Pestka, Harmonic oscillators in relativistic quantum mechanics, *Theoret. Chem. Acc.* xx (2007) xx-xx.

Paired orbitals for different spins equations

Igor Zilberberg

Boreskov Institute of Catalysis, Novosibirsk 630090, Russian Federation

A modification of standard spin-polarized Hartree-Fock or Kohn-Sham equations to make spin-up and spin-down orbitals paired will be presented. Obtained (PODS) equations are equivalent to non-canonical standard unrestricted equations in which orbital sets for alpha and beta electrons are required to be biorthogonal. The latter condition is shown to result in replacing Fock (Kohn-Sham) operator for either spin by effective operators constructed on base of Adams-Gilbert and Edmiston-Ruedenberg approach for localized orbitals.

PODS equations seem to be especially useful when used along with Noodleman broken-symmetry approach to treat antiferromagnetically coupled spins in large systems. Possible applications of developed equations to the systems of such type will be discussed.

Enhancements of the Hybrid LSCF/MM method and its Applications to Biochemical problems

Xavier Assfeld (Xavier.Assfeld@cbt.uhp-nancy.fr)

Co-workers: Delphine Bas (Delphine.Bas@cbt.uhp-nancy.fr)
Pierre-François Loos (Pierre-Francois.Loos@cbt.uhp-nancy.fr)

Chimie et Biochimie Théoriques, UMR CNRS-UHP 7565, Nancy-Université, BP 239, 54506 Vandoeuvre-lès-Nancy Cedex, France

To deal with macromolecular systems hybrid methods, mixing Quantum Mechanics and Molecular Mechanics, are nowadays certainly the only practical tool available. These methods differ from one another by of course the level of theory used for the QM part and the chosen Force Field of the MM method, but mainly by the way they handle the frontier between the QM and MM fragments. In this lecture, I will recall quickly the very basic principles on which our method [1] is based. It will be discussed, criticized objectively (as best as I can), and compared to other methods. Once the drawbacks are identified, new enhancements [2,3] will be proposed and tested.

Finally, three different applications on real systems will be presented. The first one concerns core-excited and core-ionized states of macromolecules [4]. The second one revisits the Macrophomate synthase as a candidate as a Diels-Alderase [5]. The last one will show the influence of the surrounding on the single-strand breaks induced by low-energy electrons in DNA [6].

[1] "Specific Force Field Parameters Determination for the Hybrid ab initio QM/MM LSCF method." N. Ferré, X. Assfeld and J.-L. Rivail, *J. Comp. Chem.* **23**(6) (2002) 610.

[2] "Frozen core orbitals as an alternative to specific frontier bond potential in hybrid Quantum Mechanics/Molecular Mechanics methods." A. Fornili, P.-F. Loos, M. Sironi and X. Assfeld, *Chem. Phys. Lett.* **427**, 1-3 (2006) 236-240.

[3] "On the suitability of strictly localized orbitals for hybrid QM/MM calculations." A. Fornili, Y. Moreau, M. Sironi, and X. Assfeld, *J. Comp. Chem.* **27** (2006) 515.

[4] "Core-ionized and core-excited states of macromolecules." P.-F. Loos and X. Assfeld, *Int. J. Quant. Chem.* Early view.

[5] "Macrophomate synthase: QM/MM simulations address the Diels-Alder versus Michael-Aldol reaction mecanism." C. R. W. Guimarães, M. Udier-Blagovic, and W. L. Jorgensen, *J. Am. Chem. Soc.* **127** (2005) 3577.

[6] "Electron attachment-induced DNA single strand breaks: $C_{3'}$–$O_{3'}$ σ-bond breaking of pyrimidine nucleotides predominates." J. Gu, J. Wang, J. Leszczynski, *J. Am. Chem. Soc.* **128** (2006) 9322.

Energetic crystallography: New approaches and results

K.A. Lyssenko, M.Yu. Antipin

A.N. Nesmeyanov Institute of Organoelement Compounds RAS, 119991, Vavilov Str., 29, Moscow, Russia, kostya@xrlab.ineos.ac.ru

In the lecture we will introduce the new approach and some results of systematical investigations focused on analysis of the nature and estimation of the energy of various binding interatomic interactions in crystals. The above approach is based on topological analysis of the electron density distribution function $\rho(\mathbf{r})$ obtained from the high-resolution X-ray diffraction (XRD) data by means of Bader's "Atoms in Molecule" (AIM) theory. We will demonstrate that the usage of the AIM formalism in conjunction with accurate XRD experiment makes possible to distinguish the binding interatomic interactions from all other contacts and to estimate their energy on the basis of the potential energy density function $v(\mathbf{r})$ value in the corresponding bond critical point CP (3,-1).

The current method does not need any empirical parameters and definition what number of contacts to include in calculation. It is not based on some assumption but is defined strictly by number of observed CP (3,-1) with the consequent summation of energies of all independent interactions for which CP's and bond paths are located

The developed approach provides significantly expanded information available from XRD data and makes it possible to describe interaction not on qualitative level but rather on the quantitative (energetic) one.

In particular, the usage of the current approach for analysis of interatomic interactions make it possible to:

1) Develop the method for estimation of intra- and intermolecular H-bonds formed by various donor and acceptors of hydrogen.[1a]

2) Find out the influence of intramolecular interactions on molecular electronic structure and stabilization of particular molecular conformation.[1b]

3) Estimate energy of various intermolecular interactions including previously unknown in literature, such as B…π-system, N_3…N_3, O.....("banana" bond), as well as interactions the analysis of which by *ab initio* calculation is still problematic, for e.g. H_2O…H_2O (in polyhydrates), stacking interactions, Cl^-…Cl^-, NO_3^-…NO_3^-, CO_3^{2-}…CO_3^{2-}, and Eu-O, etc. [1b-c]

The accuracy of this approach for analysis of binding inter- or intramolecular interactions was additionally approved by means of estimation the lattice energy which values in most cases were more accurate that results of periodic DFT calculations of crystals.

Authors are grateful for financial support RFBR 06-03-32557-a.

1. (a) K.A. Lyssenko, M.Yu. Antipin *Russ.Chem. Bull.* **1** (2006) 1; (b) K.A Lyssenko, M.Yu. Antipin, D.Yu. Antonov, *ChemPhysChem* **8** (2003) 817; K.A. Lyssenko, M.Yu. Antipin, M.E. Gurskii, Yu.N. Bubnov, A.L. Karionova, R. Boese, *Chem. Phys. Lett.* **384** (2004) 40; K.A. Lyssenko, S.M. Aldoshin, M.Yu. Antipin, *Mendeleev Commun.* **3** (2004) 98; (c) I.V. Glukhov, K.A. Lyssenko, A.A. Korlyukov, M. Yu. Antipin, *Faraday Discussion* **135** (2007) 203; K.A. Lyssenko, A.A. Korlyukov, M.Yu. Antipin, *Mendeleev Commun.* 2005, 90; K.A. Lyssenko, A.A. Korlyukov, D.G. Golovanov, S.Yu. Ketkov, M.Yu. Antipin, *J. Phys. Chem.* ***A110*** (2006) 6545; K.A. Lyssenko, Yu.V. Nelyubina, R.G. Kostyanovsky, M.Yu. Antipin, *ChemPhysChem.* **7** (2006) 2453; K.A. Lyssenko, Yu.V. Nelubina, D.V. Safronov, O.I. Haustova, R.G. Kostyanovsky, D.A. Lenev, M.Yu. Antipin, *Mendeleev Comm.* (2005) 232; Yu.V. Nelubina, K.A. Lyssenko, M.Yu. Antipin, *J. Phys. Chem.* ***A111*** (2007) 1091.

Biomolecules in the gas phase: why experimentalists do need theory?

Michel Mons

Laboratoire Francis Perrin (URA CEA CNRS 2453), Service des Photons, Atomes et Molécules, CEA Saclay, Bât. 522, 91191 Gif-sur-Yvette Cedex, France

Investigating biomolecules in the gas phase has become a popular issue in experimental groups formerly involved in study of small molecules. The complete toolbox of the physicists, including laser spectroscopy, is nowadays widely used to investigate in detail large models of biomolecules or even small biomolecules. Two aspects of most recent studies will be reviewed and discussed.

The first point will focus on the flexibility of biomolecules like peptides and proteins. These molecules, characterized by an intrinsic flexibility, a complex conformational landscape and a large diversity, can be investigated in detail using modern energy-resolved optical techniques which provide an acute description of the minima of the potential hypersurface.[1] The achievements and the potentialities of laser spectroscopy in terms of determination of conformational minima and energetics,[1-4] as well as of isomerisation barriers [5] will be illustrated on the example of short peptide chains.

The second part of the talk will be devoted to energy relaxation in excited states of biomolecules following photoexcitation, as investigated by femtosecond time-resolved techniques.[6, 7] The type of information derived from these experiments, namely the lifetime and nature of the electronic states involved, will be described and compared to the theoretical investigations currently performed.

In both cases the existence of a real synergy between experimental and quantum chemistry approaches is a key point for a complete understanding of these systems, leading in fine to a mutual validation of the techniques used.

[1] Chin, W., F. Piuzzi, I. Dimicoli, and M. Mons, Probing the competition between secondary structures and local preferences in gas phase isolated peptide backbones // *Phys. Chem. Chem. Phys.* **8** (2006) 1033.

[2] Chin, W., M. Mons, J.-P. Dognon, F. Piuzzi, B. Tardivel, and I. Dimicoli, Competition between local conformational preferences and secondary structures in gas-phase model tripeptides as revealed by laser spectroscopy and theoretical chemistry // *Phys. Chem. Chem. Phys.* **6** (2004) 2700.

[3] Chin, W., J.P. Dognon, F. Piuzzi, B. Tardivel, I. Dimicoli, and M. Mons, Intrinsic folding of small peptide chains: Spectroscopic evidence for the formation of beta-turns in the gas phase // *J. Am. Chem. Soc.* **127** (2005) 707.

[4] Brenner, V., F. Piuzzi, I. Dimicoli, B. Tardivel, and M. Mons, Chirality-controlled formation of beta-turn secondary structures in short peptide chains: Gas-phase experiment versus quantum chemistry // *Angew. Chem.-Int. Edit.* **46** (2007) 2463.

[5] Zwier, T.S., Laser probes of conformational isomerization in flexible molecules and complexes // *J. Phys. Chem.* A. **110** (2006) 4133.

[6] Canuel, C., M. Elhanine, M. Mons, F. Piuzzi, B. Tardivel, and I. Dimicoli, Time-resolved photoelectron and photoion fragmentation spectroscopy study of 9-methyladenine and its hydrates: a contribution to the understanding of the ultrafast radiationless decay of excited DNA bases // *Phys. Chem. Chem. Phys.* **8** (2006) 3978.

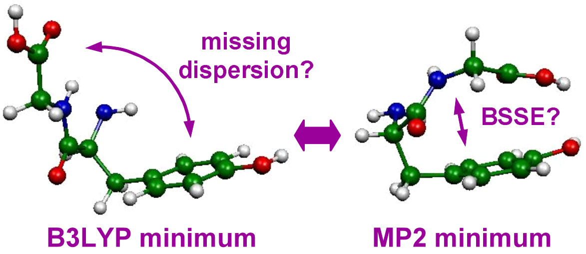
[7] Canuel, C., M. Mons, F. Piuzzi, B. Tardivel, I. Dimicoli, and M. Elhanine, Excited states dynamics of DNA and RNA bases: Characterization of a stepwise deactivation pathway in the gas phase // *J. Chem. Phys.* **122** (2005) 6.

DFT vs. MP2: which method gives the correct tyrosine-glycine structure?

Tanja van Mourik

School of Chemistry, University of St Andrews, St Andrews, United Kingdom

In previous work it was found that B3LYP and MP2, when used with the same moderately-sized basis set (6-31+G*), gave dramatically different structures for some of the conformers of the dipeptide tyrosine-glycine (Tyr-Gly) [1]: B3LYP predicted extended conformations to be more stable, whereas MP2 favoured folded structures. The very different structures obtained by these two methods are likely caused by dispersion (a true physical effect, underestimated by B3LYP) as well as large basis set superposition errors (BSSE; an artificial attraction) in the MP2 calculations [2]. Which method, if any, gives the correct structure for these conformers?



In this presentation I will show that neither B3LYP nor MP2 with small to medium-sized basis sets gives correct results for this conformer, thereby providing a stark warning against the use of these popular methods to study molecular systems where the dispersion contribution may be large. Reliable potential energy surfaces can however be obtained by reducing the BSSE in the MP2 calculations [3].

[1] D. Toroz, T. van Mourik: The structure of the gas-phase tyrosine-glycine dipeptide. *Mol. Phys.* **104** (2006) 559-570.
[2] T. van Mourik, P.G. Karamertzanis, S.L. Price: Molecular conformations and relative stabilities can be as demanding of electronic structure method as intermolecular calculations. *J. Phys. Chem.* A **110** (2006) 8-12.
[3] L.F. Holroyd, T. van Mourik: Insufficient description of dispersion in B3LYP and large basis set superposition errors in MP2 calculations can hide peptide conformers. *Chem. Phys. Lett.* (submitted).

Temporary Negative Ions – Application of Theory to Biological Molecules

J. Urban[a], P. Mach[a], P. Papp[a] and V. Staemmler[b]

[a]*Faculty of Mathematics, Physics and Informatics, Comenius University, Bratislava, Slovakia*

[b]*Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, Bochum, Germany*

Theoretical treatment of dissociative electron attachment (DEA) cannot be done by means of standard quantum chemical methods. The reason is that in the first step of DEA an electron is attached vertically to the target molecule forming an anion, which in most cases is not stable. This short time living temporary anion represents a resonance state embedded in the continuum of scattering states, thus the application of standard techniques inevitably leads to a neutral molecule plus a free electron. This is the reason why many theoretical papers based on standard methods failed in the calculation of vertical electron affinities of halogenated molecules.

In the contribution the mostly used approaches for the study of temporary negative ions are summarized and the simple scheme for the calculation of the resonance energies and resonance widths of temporary anions is proposed. The method is applied to amino acids, where the effect of secondary electrons may cause the formation of negative and positive ions and may play important role in the radical formation. The results for DEA to glycine, alanine and valine are compared with the values obtained for these molecules from the experimental study of Aflatoni et al. [1] and with results where also fragmentation reactions were observed [2].

[1] G.K. Aflatooni, B. Hitt, G.A.Gallup and P.D.Burrow, *J. Chem. Phys.* **115** (2001) 6489.
[2] P.Papp, J. Urban, S. Matejcík, M. Stano and O. Ingolfsson, *J. Chem.Phys.* **125** (2006) 204301.

Beyond the Ground State: Excited State Properties of DNA Components

Jerzy Leszczynski

Computational Center for Molecular Structures and Interactions and
Jackson State University, Jackson, MS 39217-0510, USA, E-mail: Jerzy@ccmsi.us

It is well known that genetic information is stored in DNA in the form of specific hydrogen bonding patterns between purine and pyrimidine bases. DNA components certainly are among the most elaborated biomolecules, and details of their activity are far from being completely understood. Minor tautomers of bases are suggested to cause mutation. Nucleic acid bases absorb UV radiation efficiently, but absorbed energy is quickly dissipated in the form of nonradiative decays. Although, the exact mechanism is still not known, but is becoming evident that excited state structural nonplanarity plays an important role.

The structure, function and dynamics of nucleic acid molecules are influenced by a variety of factors. The talk covers the results of recent high level ab initio studies on effects of hydration on singlet excited state structure of guanine and excited state structures of DNA bases and base pairs. It has been found that excited state dynamics would significantly depend upon environment.

Exploring physical nature of intermolecular interactions in biomolecules

W.Andrzej Sokalski and Edyta Dyguda-Kazimierowicz

Molecular Modeling and Quantum Chemistry Laboratory http://puffin.ch.pwr.wroc.pl/mml

Wroclaw University of Technology, Wyb. Wyspianskiego 27, 50-370 Wroclaw, Poland

Intermolecular interactions govern numerous properties of matter responsible among others for highly specific recognition of biomolecules and extremely high catalytic activity of enzymes. Deeper understanding of corresponding interactions forms a basis for rational design of novel molecular materials [1]. Results of two corresponding case studies are presented below.

Urokinase-type plasminogen activator (uPA) is a trypsin-like serine protease that plays a crucial role in angiogenesis process. For a group of potent phosphonic inhibitors of urokinase, flexible docking calculations were performed to gain an insight into the active site interactions responsible for observed enzyme inhibition. The docking results are consistent with the previously suggested mode of inhibitors binding. Subsequently, rigorous ab initio study of binding energy was carried out [2], followed by its decomposition defined according to the variation–perturbation procedure [3] to reveal stabilization energy constituents with clear physical meaning. Availability of the experimental inhibitory activities and comparison with theoretical binding energy allows for the validation of theoretical models of inhibition, as well as estimation of the possible potential for binding affinity prediction. Since the docking results accompanied by molecular mechanics optimization suggested that several crucial active site contacts were too short, the optimal distances corresponding to the minimum ab initio interaction energy were also evaluated. Despite the deficiencies of force field-optimized enzyme-inhibitor structures, satisfactory agreement with experimental inhibitory activity was obtained for the electrostatic interaction energy, suggesting its possible application in the binding affinity prediction.

Intermolecular interactions within the active site of 4-methyl-5-β-hydroxyethylthiazole kinase (ThiK) have been analyzed within the DTSS approach [4-5]. The role of particular ThiK residues was investigated in terms of their ability to preferentially stabilize the transition state relative to substrates (differential transition state stabilization, DTSS) or products (differential product stabilization, DPS). It seems that Mg2, Glu126 and Cys198 play a major catalytic role, whereas Mg1 and the same Cys198 are responsible for product release. Determination of catalytic fields expressing differential electrostatic potential of the transition state with respect to substrates revealed the optimal electrostatic features of an ideal catalyst for the studied reaction. The predicted catalytic environment is in agreement with experimental data showing increased catalytic activity of ThiK upon mutation of Cys198 to aspartate [6].

[1] Molecular Materials with Specific Interactions: Modeling and Design, (W. A. Sokalski -Ed) Vol. 4, Series: Challenges and Advances in Computational Chemistry and Physics (J. Leszczynski-Ed), Springer, 2007, ISBN: 978-1-4020-5371-9, 598 pp, http://www.springer.com/west/home?SGWID=4-102-22-173674027-0

[2] R. Grzywa, E. Dyguda-Kazimierowicz, M. Sieńczyk, M. Feliks, W. A. Sokalski, J. Oleksyszyn, *J.Mol.Model.*, in press, DOI: 10.1007/s00894-007-0193-8.

[3] W.A. Sokalski, S. Roszak, K. Pecul, *Chem.Phys.Lett.* **153** (1988) 153.

[4] W.A. Sokalski, *J.Mol.Catal.* **30** (1985) 395.

[5] B. Szefczyk, A.J. Mulholland, K.E. Ranaghan, W.A. Sokalski, *J.Am.Chem.Soc.* **126** (2004) 16148.

[6] E. Dyguda-Kazimierowicz, W. A. Sokalski, J. Leszczyński, *J.Mol.Model.*, in press, DOI: 10.1007/s00894-007-0192-9.

Structure and intramolecular hydrogen bonding in canonical 2'-deoxyribonucleotides

Oleg V. Shishkin[a,d], Leonid Gorb[b,c], Jerzy Leszczynski[b]

[a]STC "Institute for Single Crystals", National Academy of Science of Ukraine, 60 Lenina ave., Kharkiv 61001, Ukraine

[b]Computational Center for Molecular Structure and Interactions, Department of Chemistry, Jackson State University, P.O. Box 17910, 1325 Lynch Street, Jackson, MS 39217, USA

[c]Department of Molecular Biophysics, Institute of Molecular Biology and Genetics, National Academy of Science of Ukraine, 150 Zabolotnogo str., Kyiv 03143, Ukraine

[d]Ukrainian-American Laboratory of Computational Chemistry, Kharkiv, Ukraine, Jackson, MS, USA

Canonical 2'-deoxyribonucleotides represent the main building blocks of DNA. They are very flexible molecules and their structure significantly depends on nature of base and subtle balance of intramolecular interactions.

Theoretical investigation of molecular structure of monophosphates of 2'-deoxythymidine (TMP), 2'-deoxycytidine (CMP), 2'-deoxyguanosine :GMP) and 2'-deoxyadenosine (AMP) using density functional theory reveals that conformational properties of these molecules are tuned mainly by uncompensated negative charge of the phosphate group and intramolecular interactions between phosphate group and base. Ribose moiety play a role of soft buffer between these fragment and it easily change its conformation in order to provide the most suitable conditions for intramolecular interactions. This properties of sugar linkage manifests itself especially in the case of syn conformers of CMP and AMP which is stabilized by intramolecular N-H…O hydrogen bond between amino group of bases and phosphate group. The same conclusion is made for complexes of GMP with hydrated magnesium cation.

Comparison of geometrical parameters of isolated nucleotide4s and average values for different types of DNA indicates that incorporation of nucleotides to A-DNA requires the smallest changes of conformation and increase of energy. In the case of B, C and D-DNA energy of nucleotides deformation is significantly higher (up to 10 kcal/mol per nucleotide).
Introduction of second phosphate group results in significant unification of conformation of backbone in all nucleotides. Protonation of the nitrogen atoms of bases cause drastical change of relative stability of conformers and deformation of ribose conformation.

Topological analysis of the electron density distribution reveals existence of set of intramolecular hydrogen bonds in nucleotides. The C6-H…O H bonds in pyrimidine nucleotides and C8-H…O H bonds in purine nucleotides exists in all conformers with anti orientation of base and may be considered as reference hydrogen bonds. They clearly demonstrate charge assisted character. Increase of uncompensated negative charge of the phosphate group leads to considerable strengthening of these interactions.

Protonation of bases results in transformation of rather weak C-H…O hydrogen bonds to extra strong H-bonds with characteristics which are close to strong conventional hydrogen bonds. This also creates opportunities for proton transfer between the C6/C8 atom of base and the oxygen atom of phosphate group. In some cases protonation also is accompanied by proton transfer from nitrogen atoms of bases to phosphate group leading to change of tautomeric form of nucleobase.

Molecular Dynamics simulations as a unique tool to study functional RNAs

Jiří Šponer

Institute of Biophysics, Academy of Sciences of the Czech Republic, Královopolská 135, 61265 Brno, Czech Republic, sponer@ncbr.chemi.muni.cz

MD simulation technique captures qualitative differences in intrinsic flexibilities of ribosomal RNA (rRNA) building blocks possessing contrasting intrinsic flexibility signatures. The basic intrinsic physico-chemical properties of the RNA motifs can in many cases be maintained in the RNA assemblies and contribute to function and sequence constraints. Kink-turns show profound elbow-like intrinsic flexibility, without disruption of any single structural feature characteristic of a folded K-turn. The K-turn oscillatory dynamics is typically pivoting at the A-minor base quartet mediating the contact between the *C*- and *NC-stems*, is associated with a dynamical water insertion into the A/C basepair and the motion is anharmonic. Such structural elements are well suited to passively mediate large-scale motions. The Sarcin-Ricin loop is very stiff in simulations and also the Loop E is rigid. Helix 44 from the small subunit is an isotropic flexible element with modest sequence-dependence of elasticity along the helix and a possible structural basepairing switch at its base. Consecutive RNA building blocks can further create architectures with complex patterns of preferred low-energy motions, as in the Helix 42-44 portion of the 23S rRNA (abbreviated as Kt-42+rGAC; Kink-turn 42 and GTPase associated center rRNA). The bottom part of this molecule consists of alternating rigid and flexible segments. The first flexible segment (*Hinge1*) is Kt-42. The second one (*Hinge2*) is localized at the junction between Helix 42 and Helices 43/44. The rigid segments are the two arms of Helix 42 flanking the Kink. Overall, the Helix 42-44 rRNA is constructed as a sophisticated intrinsically flexible anisotropic molecular nano-arm. Variation of the length of stems of Helix 42 would considerably change the direction of anisotropic flexibility. Indeed, we found that Helix 42 length is 100% conserved throughout the evolution and when mitochondria and chloroplasts are considered, Helix 42 is among the ~30% of the entirely length-conserved ribosomal helices. I will also demonstrate that simulations are capable to provide unique insights into the structural dynamics of small catalytic RNAs, and contrast our results for the Hepatitis Delta Virus and Hairpin ribozymes.

[1] Reblova, K. et al. Non-Watson-Crick basepairing and hydration in RNA motifs: Molecular dynamics of 5S rRNA loop E. *Biophys. J.* **84** (2003) 3564-3582.

[2] Razga, F. et al. Elastic properties of ribosomal RNA building blocks: Molecular dynamics of the GTPase associated center rRNA. *Nucleic Acids Res.* (2007) in press.

[3] Razga, F. et al. Hinge-like motions in RNA Kink-turns: The role of the second A-minor motif and nominally unpaired bases. *Biophys. J.* **88** (2005) 3466-3485.

[4] Reblova, K., et al. Structure, dynamics and elasticity of free 16S rRNA Helix 44 studied by molecular dynamics simulations. Biopolymers **82** (2006) 504-520.

[5] Spackova, N. and Sponer, J. Molecular dynamics simulations of Sarcin-Ricin rRNA motif. *Nucleic Acids Res.* **34** (2006) 697-708.

[6] Krasovska, MV. et al. Cations and hydration in catalytic RNA: Molecular dynamics of the hepatitis delta virus ribozyme. *Biophys. J.* **91** (2006) 626-638.

[7] Rhodes, MM. et al. Trapped water molecules are essential to structural dynamics and function of a ribozyme. *Proc. Natl. Acad. Sci. USA* **103** (2006) 3380-13385

Computational study on aquation of ruthenium(II) complexes and their interactions with DNA bases

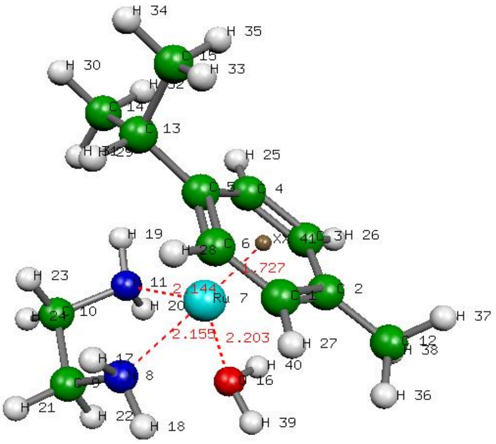
J.V. Burda and Z. Futera

Department of Chemical Physics and Optics, Charles University ,121 16 Prague 2,Czech Republic

Ru(II)-piano-stool complexes

Recently, Ru(II)-piano-stool complexes were reported as promising anticancer drugs in Sadler's group.[1, 2] Replacement reactions between $[\text{Ruthenium(II)(Arene)(en)X}]^{2+}$ complexes ($X=Cl^-$, H_2O, OH^-, guanine, adenine, cytosine, and thymine) were studied. DFT/MP2 calculations were performed in both gas phase and COSMO regimes. Bonding energies of individual ligands were determined. Relatively strong metal-arene interactions were found in comparison with DNA base coordinations.

In the supermolecular approach, reaction profile for process of the chloride replacement by water was examined. Both thermodynamic and kinetical description of this process was obtained and compared with similar process of the cisplatin activation.



[1] Aird, R.; Cummings, J.; Ritchie, A.; Muir, M.; Morris, R.; Chen, H.; Sadler, P.; Jodrell, D., *Br. J. Cancer* **86** (2002) 1652-1657.

[2] Berners-Price, S. J.; Frenkiel, T. A.; Frey, U.; Randolf, J. D.; Sadler, P. J., *J. Chem. Soc., Chem. Commun.* (1992) 789.

Nature of chemical bonds in molecular systems containing rare gas atoms

Zdzislaw Latajka

Faculty of Chemistry, University of Wroclaw, F.Joliot-Curie 14, 50-383 Wroclaw, Poland

The rare gases (Rg) are usually considered as chemically inert due to their stable electronic structure of valence electrons unfavorable to formation of chemical bonds. The inertness of rare gases has been used e.g. in the development of matrix isolation technique since the early 1950s.

The first chemical compound containing rare gas atom, $Xe^+[PtF_6]^-$, was experimentally prepared 45 years ago by Bartlett [1]. The last four decades have introduced a rich and interesting world of rare gas chemistry.

Recently, a new class of rare gas containing molecules, HRgY, have been prepared and characterized in the IR low-temperature matrices spectroscopy [2-4]. Usually molecules are experimentally prepared in low-temperature matrices by photodissociation of a hydrogen-containing precursor and thermal mobilization of the photodetached hydrogen atoms.

In order to understand the nature of chemical bonds in the molecular systems containing Rg atoms we have applied the electron localization function (ELF), which is an indirect measure of the probability of finding two electrons with the opposite spins [5]. Via ELF analysis we can obtain information of the degree of ionic and covalent bonding in studied molecules.

The results of ab initio calculations, the ELF analysis and the discussion of the nature of chemical bonds with Rg atoms will be presented for following systems:

- HRgCN and HRgNC (Rg = Ar, Kr, Xe),
- HXeOH and HXeSH,
- $(HXeH)_n$ with n =2 ÷ 4, $Xe_2H_3^+$,
- FXeSiF,
- molecular complexes - HXeOH...H_2O (Rg analogues of water dimer) and XeH_2...H_2O (example of dihydrogen bond).

[1] N.Bartlett, *Proc.Chem.Soc.*, (1962) 218.
[2] M.Pettersson, J.Lundel, M.Räsänen, *Eur.J.Inorg.Chem.*, (1999) 729.
[3] L.Khriachtchev, M.Pettersson, M.Runeberg, J.Lundell, M.Räsänen, *Nature*, **406** (2000) 874.
[4] J.Lundell, L.Khriachtchev, M.Pettersson, M.Räsänen, *Low Temp.Phys*. **26** (2000) 680.
[5] A.D.Becke, K.E.Edgecombe, *J.Chem.Phys*. **92** (1990) 5397.

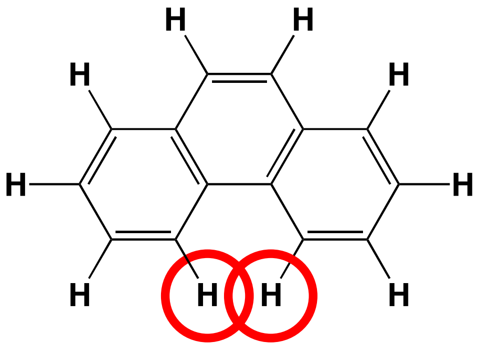
Is the H···H interaction in phenathrene responsible for its higher stability as compared to anthracene?

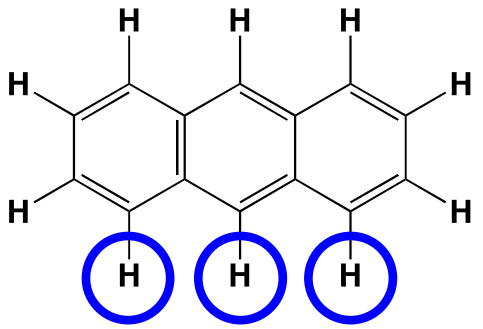
Miquel Solà[a], Jordi Poater[b] and F. Matthias Bickelhaupt[b]

[a] ***Institut de Química Computacional and Departament de Química, Universitat de Girona, Campus Montilivi, E-17071 Girona, Catalonia, Spain***

[b] ***Afdeling Theoretische Chemie, Scheikundig Laboratorium der Vrije Universiteit, De Boelelaan 1083, NL-1081 HV Amsterdam, The Netherlands***

Based on an atoms-in-molecules (AIM) analysis, Matta et al. (*Chem. Eur. J.* **2003**, *9*, 1940) recently claimed evidence for the existence of hydrogen–hydrogen bonding interactions in polycyclic aromatic hydrocarbons (PAHs) such as biphenylene, kekulene, phenanthrene, chrysene or benzanthracene. In particular, they concluded that H···H bonding interactions between the hydrogen atoms bonded to the 1,4-carbon atoms of the bay region of phenanthrene are responsible for the larger stability of this molecule as compared to anthracene. This conclusion is opposed to many accumulated evidences of nonbonded steric repulsions between these two hydrogen atoms. In the present work [1-4], we address the question whether H···H bonding in phenanthrene exists, as suggested by AIM, or not by means of density functional theory (DFT) at the BP86/TZ2P level of theory and we provide new convincing proofs on the repulsive character of the H···H interactions between *ortho*-hydrogens in the bay region of phenanthrene. We conclude that phenanthrene is more stable than anthracene due to more efficient π-bonding, not H···H bonding. Our results falsify the hypothesis of H···H bonding and show that "bond paths" and "bond critical points" are not good indicators of a stabilizing interaction.





[1] J. Poater, M. Solà and F. M. Bickelhaupt, *Chem. Eur. J.* **12** (2006) 2889-2895.
[2] J. Poater, M. Solà and F. M. Bickelhaupt, *Chem. Eur. J.* **12** (2006) 2902-2905.
[3] J. Poater, R. Visser, M. Solà and F. M. Bickelhaupt, *J. Org. Chem.* **72** (2007) 1134-1142.
[4] J. Poater, F. M. Bickelhaupt and M. Solà, *J. Phys. Chem. A*, submitted.

Theoretical study of the structure of HO_n and H_2O_n species in water

M.T.C. Martins Costa[a], S. Chalmet[a], A. Mansergas [b], J.M. Anglada[b]
and M.F. Ruiz-López[a]

[a]SRSMC, Nancy-University, BP 239, 54506 Vandoeuvre-les-Nancy, France

[b]Theoretical and Computational Chemistry Group, IIQAB–CSIC. c/ Jordi Girona 18, E-08034 Barcelona, Spain

The key role played by ozone in the atmosphere is well known but industrial applications of this molecule are important too. For instance, ozone provides an environment-friendly solution in wastewater treatment, bleaching of paper pulp or air disinfection. Applications in medicine are also very promising due to ozone's ability to destroy microorganisms and regulate the immune system. The processes of interest often take place in aqueous solution where ozone decomposes through a complex mechanism that involves initial reaction with a hydroxide ion followed by formation of a variety of oxidizing species. HO, HO_2, as well as hydrogen peroxide H_2O_2, are certainly the most prominent ones but formation of HO_3, HO_4 and H_2O_3 has been suggested as well. Only very recently, the structures of HO_3 and H_2O_3 have been experimentally determined in gas phase while H_2O_3 has been detected in solution. In contrast, the existence of the HO_4 radical is still the object of controversy. Higher order polyoxides H_2O_n ($n \geq 4$) have been theoretically investigated though only the smallest member of this series has been experimentally prepared.

In this work, we have studied the structure of these species in water solution through Molecular Dynamics simulations using a combined Quantum Mechanics and Molecular Mechanics approach. The presentation will include previously published results on HO, HO_2, HO_3 and H_2O_2 (1-3) as well as recent data on HO_4 and hydrogen polyoxides.

[1] S. Chalmet and M. F. Ruiz-López, *J. Chem. Phys.* **124** (2006) 194502.
[2] S. Chalmet and M. F. Ruiz-Lopez, *ChemPhysChem* **7** (2006) 463-467.
[3] M. T. C. Martins-Costa and M. F. Ruiz-López, *Chem. Phys.* **332** (2007) 341-347.

Structural, spectroscopic and magnetic properties of MeOOH minerals (Me=Al, Mn, Fe)

Daniel Tunega[a,b]

[a]Institute for Theoretical Chemistry, University of Vienna, Währingerstrasse 17, A-1090, Vienna, Austria

[b]Institute of Soil Research, University of Natural Resources and Applied Life Sciences, Vienna, Peter-Jordan-Strasse 82b, A-1190 Vienna, Austria

Metal oxyhydroxides, MeOOH, are minerals, which can be used in a variety of industrial applications like catalysts, sorbents, pigments or magnetic devices. Moreover, goethite (α-FeOOH) is an important soil mineral actively acting in soil processes or it can also be found in products of corrosion. This work reports a theoretical study of structural, spectroscopic and magnetic properties of the MeOOH minerals. Density functional theory (DFT) based on the LDA-GGA approximation was used in the study. It was found by spin-polarized DFT calculations that $3d$-metal oxyhydroxides are the most stable in the antiferromagnetic, high-spin configuration. However, the study of the isostatic pressure compression showed that at high pressures the high-spin configuration collapsed due to the increasing on-site Coulomb repulsion among the localized $3d$ electrons. Thus, an adapted sp-DFT+U method was used instead of the “standard” sp-DFT approach. It was found that the sp-DFT+U method has to be used for a correct description of the spin states of $3d$-metal oxyhydroxides, especially in the range of high pressures. Bulk modulus parameters were calculated by fitting the Birch-Murnaghan equation of states and a very good agreement between experimental and computed values was found. Some uncertainties in the interpretation of the experimental IR spectrum of the groutite (α-MnOOH) were explained on the base of the calculated theoretical spectrum. A very narrow splitting of stretching vibrations of hydroxyl groups was found.

DYNAMICS ON THE NANOSCALE:
Time-domain ab initio studies of carbon nanotubes, quantum dots, and molecule-semiconductor interfaces

Oleg Prezhdo

University of Washington, Seattle, USA

Device miniaturization requires an understanding of the dynamical response of materials on the nanometer scale. A great deal of experimental and theoretical work has been devoted to characterizing the excitation, charge, spin, and vibrational dynamics in a variety of novel materials, including carbon nanotubes, quantum dots, conducting polymers, inorganic semiconductors and molecular chromophores. We have developed state-of-the-art non-adiabatic molecular dynamics techniques and implemented them within time-dependent density functional theory in order to model the ultrafast photoinduced processes in these materials at the atomistic level, and in real time.

The electron-phonon interactions in carbon nanotubes (CNT) determine the response times of optical switches and logic gates, the extent of heating and energy loss in CNT wires and field-effect transistors, and even a superconductivity mechanism. Our ab initio studies of CNTs directly mimic the experimental data and reveal a number of unexpected features, including the fast intrinsic intraband relaxation and electron-hole recombination, the importance of defects, the dependence of the relaxation rate on the excitation energy and intensity, and a detailed understanding of the role of active phonon modes.

Quantum dots (QD) are quasi-zero dimensional structures with a unique combination of molecular and bulk properties. As a result, QDs exhibit new physical properties such as carrier multiplication, which has the potential to greatly increase the efficiency of solar cells. The electron-phonon and Auger relaxation in QDs compete with carrier multiplication. Our detailed studies of the competing processes in PbSe QDs rationalize why carrier multiplication was first observed in this material.

Electron transfer across molecular/bulk interfaces is the subject of active research, creating many challenges due to the stark differences between the quantum states of molecules and periodic systems, as well as the often disparate sets of theories and experimental tools used by chemists and physicists. Charge transport across the interface remains is a key to such fields as molecular electronics, photo-catalysis, electrolysis, and photo-voltaics. The theoretical studies provide an exclusive perspective on the photoinduced interfacial transfer dynamics.

Our real-time atomistic simulations create a detailed picture of these materials, allow us to compare and contrast their properties, and provide a unifying description of quantum dynamics on the nanometer scale.

Structural and thermodynamic properties of microclusters – precursors of germanium/carbon and germanium/silicon nanomaterials

Szczepan Roszak and Pawel Wielgus

Institute of Physical and Theoretical Chemistry, Wroclaw University of Technology, Wybrzeze Wyspianskiego 27, 50-370 Wroclaw, Poland

Studies of germanium/silicon and germanium/carbon compounds are of technological interest because of their practical applicability in the semiconductor industry. Direct applications of the Ge/X (X=C, Si) technology comprehend high-frequency transistors, photodiodes and infrared photodetectors, and solar cells. Nanocrystals of Ge have received a lot of interest in resent years. Self-organized quantum dots of Ge have been grown on Si substrates. Under growth conditions interdiffusion between C, Si and Ge may occur to form alloy as was observed in Ge/Si superlattices and in Ge quantum dots grown on Si. In order to understand spontaneous processes leading to the self-organized quantum structures detailed knowledge of thermodynamics and nature of Ge-Si bonding is needed. The theoretical solid state studies taking into account materials with present Ge-Si and Ge-C bonds are scarce. The Ge/C and Ge/Si chemistry of small compounds is very restricted comparing to vast data on solid state materials. Theoretical studies on the Ge_nC_m and Ge_nSi_m (n=1,2; m=1-3) micro-clusters have been performed using the state of the art calculations. Several alternative structures of these clusters were studied to locate the lowest energy isomers. It is observed that the structures of the complexes result from the competition between ionic Ge-C (Ge-Si), conjugated covalent C-C (Si-Si), and metallic Ge-Ge bonds. The ionization of the molecules enhances the ionic character of the Ge-C (Ge-Si) bond and has significant structural consequences. Using theoretically determined partition functions, thermodynamic data are computed and experimental enthalpies are enhanced. The *ab initio* atomization energies of (germanium + carbon) and (germanium + silicon) heterostructures compare well with corrected experimental functions. The experimental appearance potentials are well reproduced by the theoretical ionization potentials.

Distributed Gaussian Basis Sets:
Recent Progress and Future Prospects

S. Wilson[a], V.N. Glushkov[b] and O.S. Belkina[b]

[a]***Physical & Theoretical Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QZ, England***

[b]***Physics Department, National University of Dnepropetrovsk, per. Nauchniy 13, 49050, Dnepropetrovsk, Ukraine***

Recent progress in the development of distributed Gaussian basis sets [1] for molecular electronic structure calculations is reviewed with particular emphasis on: (i) variationally optimized sets [2], (ii) distributions based on harmonic and anharmonic models [3], (iii) comparisons with finite difference Hartree-Fock calculations for diatomic molecules [4], (iv) application to the relativistic molecular electronic structure problem [5].

The future prospects of the distributed Gaussian basis set approach are discussed concentrating on: (i) the control of linear dependence and the Cholesky decomposition of the two-electron integral matrix, (ii) direct second order energy minimization, (iii) the development of a compact computer program using literate programming methodology and exploiting parallel processing, (iv) the description of electron correlation effects in molecules.

[1] S. Wilson, in *New Methods in Quantum Theory*, ed. C.A. Tsipis, V.S. Popov, D.R. Herschbach and J.S. Avery, NATO Advanced Study Institute, Series 3 - High Technology volume 8, p. 437, Kluwer Academic Publishers, Dordrecht (1996).
[2] V.N. Glushkov and S. Wilson, *Adv. Quant. Chem.* **39** (2001) 123; *Int. J. Quant. Chem.* **89** (2002) 237; *Int. J. Quant. Chem.* **99** (2004) 903.
[3] V.N. Glushkov and S. Wilson, *Int. J. Quant. Chem.* (in press).
[4] V.N. Glushkov, J. Kobus and S. Wilson, *Int. J. Quant. Chem.* (submitted for publication).
[5] H.M. Quiney, V.N. Glushkov and S. Wilson, *Int. J. Quant. Chem.* **89** (2002) 227.

Application of Quantum Trajectory Method for Multidimensional Reactive Scattering

Dmytro Babyuk[a] and Robert E.Wyatt[b]

[a] ***Chernivtsy National University, Ukraine***

[b] ***University of Texas at Austin, USA***

Over the past decade, significant progress has been reported in the development and application of quantum mechanical methods for chemical reaction dynamics. Quantum trajectory method (QTM) provides time-dependent reaction dynamics and is quite different from the conventional approaches. An important feature of this method is that the minimum number of trajectories required for stable propagation scales linearly with the number of degrees of freedom. For systems where the potential surface is modeled by a Gaussian barrier along the translational coordinate coupled to M vibrational coordinates represented by harmonic oscillators, the QTM permits computations on multidimensional quantum reactive systems with as many as 200 harmonic vibrational degrees of freedom. Spatial derivatives needed in the equations of motion are evaluated by means of least squares fitting. Unlike conventional grid methods where each degree of freedom must be discretized at fixed constant values for all remaining coordinates thus leading to exponential scaling between the total number of grid points and the number of degrees of freedom, the quantum trajectory method uses an irregular mesh defined by the trajectory locations. In this case, the scaling of computational effort is determined by the basis set size used in the least squares fitting procedure. In this study, a special set of reaction path coordinates was developed and used.

The model was initially tested on system with a moderate number of vibrational modes ($M \leq 25$) and then the dimensionality was extended to 200 vibrational modes. The maximum number of trajectories used was N=5000. The computer time at this fixed N increases with M according to a power law with the exponent lower than 2. For the case of one vibrational mode, the dynamical results were in good agreement with those obtained by integration of the time-dependent Schrödinger equation on a fixed grid. The harmonic oscillators in the potential energy significantly simplify basis set design for the least squares fitting routine. For the vibrational coordinates, the basis set, which is restricted to second-order terms, provides a perfect fit. Moreover, this basis even permits the use of fitting coefficients derived for a reference point for a set of points close to it. However, even small vibrational anharmonicities quantitatively change the dynamics of ensembles of quantum trajectories. The basis set for least square fitting must be extended and at least include third-order terms. For the model with Morse vibrational potential which is closer to realistic systems, computations were done for the case of 25 vibrational degrees of freedom.

Analyzing Molecular Excited States within Time-Dependent Density Functional Theory

A.V. Luzanov, O.A. Zhikol

SSI "Institute for Single Crystals" National Academy of Sciences of Ukraine, 61001 Kharkiv, 60 Lenin ave., and

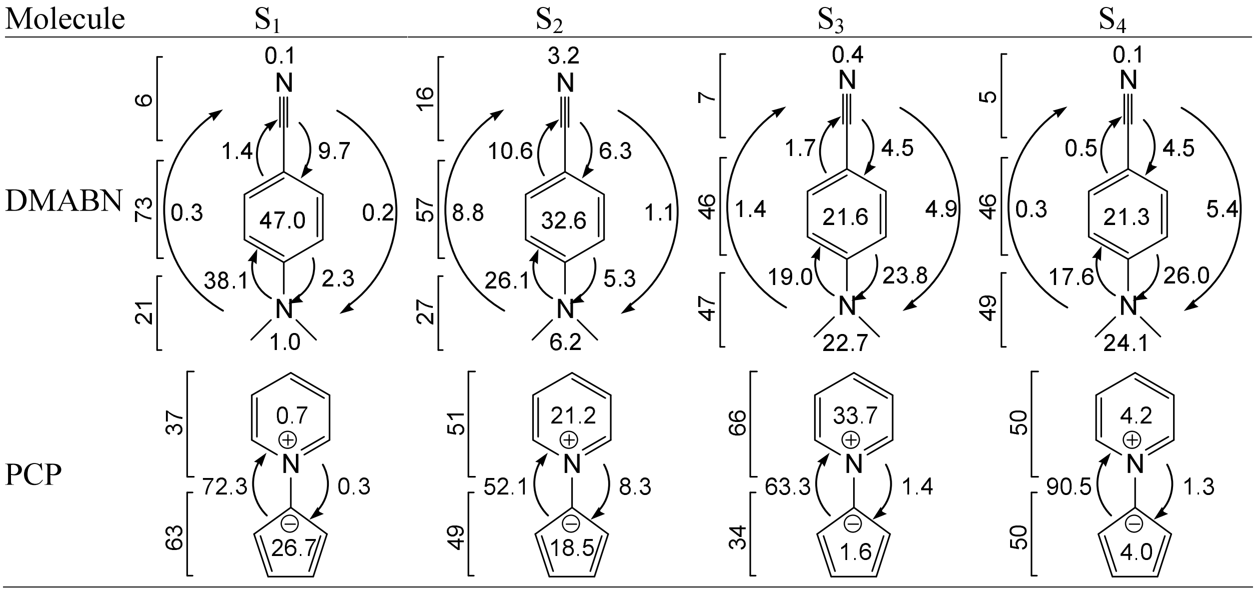
Ukrainian-American Laboratory for Computational Chemistry, Kharkiv, Ukraine – Jackson, USA

In the last decade it was shown that time-dependent density functional theory (TD-DFT) is sufficiently reliable for excited atoms and molecules [1]. Among the tools proposed for a pictorial description of excited states, the so-called charge-transfer (CT) numbers and localization indices [2] are shown to be especially useful, because these physical properties are familiar to chemists. The technique given in [2] will be referred to as the excited-state structural analysis. Only the scanty data (like given in [3]) are available for using the technique at *ab initio* level of the theory.

In this report the excited-state structural analysis already known for the singly-excited configuration interaction (CIS) is extended to the TD-DFT. The TD-DFT solutions are converted to the form similar to that for the CIS method. It allows us, in particular, to consistently compute the normalized TD-DFT values of the interatomic hole-particle populations in the form of CT indices. We study CT indices and localization of the electronic excitations for the low-lying excited states in some typical conjugated systems using B3LYP functional parameterization.

As examples below are shown the results of applying the excited-state structural analysis to the molecules with known strong CT effects, viz. 4-dimethylaminobenzonitrile (DMABN) and pyridinium cyclopentadienylide (PCP).

TD-DFT charge-transfer diagrams for the lowest singlet excited states S_i of DMABN and PCP



Numbers at arrows represent the charge-transfer numbers associated with electron transfer within a molecule (normalized to 100%). Numbers at brackets represent the gross excitation indices (in %) of molecular fragments.

[1] A. Dreuw, M. Head-Gordon, *Chem. Rev.* **105** (2005) 4009.
[2] A. V. Luzanov, *Usp. Khim.* **49** (1980) 2086.
[3] A. V. Luzanov, O. V. Prezhdo, *Int. J. Quant. Chem.* **102** (2005) 582.

Magnetic structure and low-temperature thermodynamics of transition metal compounds with magnetic sublatice of ladder type

V.O. Cheranovskii, E.V. Ezerskaya

Kharkov National University 61077, Kharkov, Ukraine, cheranovskii@univer.kharkov.ua

To investigate magnetic properties of some transition metal compounds having magnetic sublattice of ladder type we treated two models of strongly correlated electrons on ladder lattices with three-site unit cells. First one is the anisotropic Heisenberg spin-1/2 model describing the ladder systems with one electron per lattice site. Second model is one-band Hubbard model with infinite electron repulsion, which describes electron systems with arbitrary filling of the band and may be of interest for investigation of the properties of some doped systems.

We studied magnetic properties of Heisenberg model on rectangular three-leg ladder and one of the simplest representatives of diagonal ladders - necklace spin ladder. Three-leg spin ladder and necklace spin ladder describe adequately magnetic structure of some perovskites like $Sr_2Cu_3O_5$ and IPA_2CuCL_4 (IPA- isopropylammonium) respectively. In the limit of weak interaction between unit cells and antiferromagnetic Ising coupling we derived a number of effective low-energy Hamiltonians for both spin ladder systems. The analysis of the spectra of these Hamiltonians shows clearly the existence of intermediate magnetization plateau in field dependence of magnetization at $M=M_s/3$ (M_s is the saturation magnetization). For intermediate interaction between unit cells and zero temperature this plateau was found by means of numerical simulation of field dependence of the magnetization of ladder clusters consisting of 18 spins (Davidson method) and density matrix renormalization group study (DMRG). Special attention was given to anisotropic necklace spin ladder. The quantum phase transition between ferrimagnetic and nonmagnetic phases in the vicinity of zero value of spin anisotropy parameter was found for this ladder. Isotropic necklace spin ladder has ferrimagnetic ground state of spin wave structure. By means of perturbation theory analysis we found that the amplitude of this spin wave as a function of inter-cell coupling should have at least one maximum. According to the exact diagonalization study and DMRG calculations, there is only one maximum, which corresponds to the ladder with equal coupling constants – ladder with spin and space isotropy.

To perform the simulation of low-temperature thermodynamics of the spin ladder models we constructed the approximate energy spectrum of the ladder as a superposition of low lying states with one inverted spin and bound states with two and three inverted spins without dispersion. The ladder partition function was derived on the base of this approximation. The exact diagonalization study of finite ladder clusters formed by 9-12 spins and approximate evaluation of temperature and field dependence of magnetization and specific heat per unit cell agree well and show the existence of magnetization plateau at low temperatures for both type of ladders. According to our simulation the increase of temperature leads to the destruction of the magnetization plateau.

We applied Hubbard model with infinite electron repulsion to investigate the effects of electron doping on low-temperature thermodynamics and magnetic structure of the three-leg rectangular ladder and necklace ladder. To derive effective low-energy Hamiltonians for both ladders with weak coupling between unit cells we applied cycle spin permutation technique and perturbation theory expansion. These Hamiltonians were used for study of the formation of magnetic polarons due to the competition of the interactions of neighbor unit cells with equal and different electron filling. In the polaron approximation we had found the conditions of the appearance of ferromagnetic ground state of infinite ladder systems. For the ladders with two electrons per unit cell the corresponding low-energy Hamiltonians have pure spin structure of non-Heisenberg type. These Hamiltonians had been used for exact diagonalization study of temperature and field dependences of magnetization, magnetic susceptibility and specific heat of finite ladder clusters formed by 12-21 lattice sites.

Quantum study of antiepileptic drugs and chemoconvulsants interaction with "key" amino acids sequences of GABA$_A$ receptor

O. Yevtushenko[a], L. Gromov[a], V. Kouts[b]

[a]*Institute of Pharmacology and Toxicology AMS of Ukraine, Eugene Potie str., 14, Kyiv 03057, Ukraine*

[b]*Institute for Sorption and Endoecology Problems NAS of Ukraine Gen. Naumov Str., 13, Kyiv 03164, Ukraine*

Introduction: GABA$_A$ receptors are the major inhibitory neurotransmitter receptors in the central nervous system. They are composed of different subunits comprising a transmembrane chloride anion channel and thereby are involved in mediating sedative, anticonvulsant activity.

The important sites for GABA and its competitive antagonists (bicuculline) binding with GABA$_A$ receptors are represented by the following amino acids residues: Ser^{156} - Tyr^{157} - Gly^{158} - Tyr^{159} - Thr^{160} - Thr^{161} (I) and Thr^{201} -Thr^{202} - Gly^{203} - Ala^{204} - Tyr^{205} - Pro^{206} (II) of β_2-subunit, and also Val^{64} - Phe^{65} - Phe^{66} - Arg^{67} (III) of α_1-subunit [Mehta A.K., Ticku M.K., 1999; Brain Research Review; 29:196-217.]. Sites for the binding of non-competitive GABA antagonists (picrotoxin, pentilentetrazole (PTZ)) with GABA$_A$ receptors are Thr^{255} - Val^{256} - Phe^{257} (IV) and Val^{262}-Leu^{263} - Thr^{264} (V) of α_1-subunit [Buhr A., et.al 2001; J Biol Chem; 276(11):7775-81.]

Results: Using bicuculline, PTZ, picrotoxin seizure tests on non-linear adult albino mice the row of activity for widely used in clinic antiepileptic drugs (AED) was composed: Felbamate > Phenobarbital > Carbamazepine> Lamotrigine > Valproic acid > Topiramat (test with bicuculine); Valproic acid > Phenobarbital > Felbamate > Carbamazepine > Topiramat > Lamotrigine (test with PTZ); Carbamazepine > Lamotrigine > Felbamate > Topiramat > Phenobarbital > Valproic acid (test with picrotoxin). The drugs were used in the doses of 1/10 from LD50. One-way ANOVA (StatSoft Statistica 6.0.) was applied for statistical calculations.

By quantum-chemical semi-empirical method AM1 (program HyperChem7) the most active centres of the key amino acids sequences were determined. The analysis of the functions of local electronic density states on amino acids (I-V) has shown that for the active binding sites for bicuculline: in (I) — Tyr^{157}, Tyr^{158}, Thr^{161}; in (II) — Thr^{201}, Thr^{202}, Tyr^{205}; in (Ш) — Phe^{65}, Phe^{66}; for PTZ and picrotoxin: in (IV) — Phe^{257}; in (V) — Leu^{263} which supports the literature data. The binding energy of the examined AED and convulsants with amino acid sequences I-V ($\Delta E = E_{am/ac.,AED.,conv} - E_{am/ac.} - E_{AED.,conv.,}$) was calculated. The correlation between the activity of anticonvulsants in vivo with bicuculine and binding energy ΔE for amino acid sequence Thr^{201} -Thr^{202} - Gly^{203} - Ala^{204} - Tyr^{205} - Pro^{206} (II) was correlated with the activity of anticonvulsants in vivo. $\Delta E = -1.3 \times F - 0.9$, $r=0.974$, $n = 5$, Fisher parameter (F), that characterize the AED degree of activity.

Conclusions: The results obtained could be used for the purposeful search of antiepileptic drugs with improved anticonvulsant activity. The criteria for such search could be the energy of interaction between anticonvulsants and structural units of GABA$_A$ receptor, Thr^{202} - Gly^{203} - Ala^{204} - Tyr^{205} - Pro^{206} in particular.

All experiments were carried out according to "Guide for the Care and Use of Laboratory Animals" (National Academy Press, USA, 1996), with the permission of Biological Ethics Commission of the Institute of Pharmacology and Toxicology AMS, Ukraine for the work with Laboratory Animals.

The Propensity of Gold Clusters To Form Nonconventional X-H···Au Hydrogen Bonds with DNA Bases and Watson-Crick Base Pairs

Eugene S. Kryachko

Bogoliubov Institute for Theoretical Physics, Kiev-143, 03680 Ukraine and

Department of Chemistry, Bat. B6c, University of Liege, B-4000 Liege, Belgium

We summarize the computational evidence that gold clusters can behave as ‘nonconventional’ proton acceptors and form a new type of ‘nonconventional’ hydrogen bonding with the conventional proton donors, which satisfies all necessary and sufficient conditions of the classical or conventional hydrogen bonding [1-7]. The origin of this nonconventional hydrogen bonding interaction is investigated on the complexes which gold clusters $Au_{1\leq m\leq 8,20}$, including the tetrahedral cluster Au_{20}, form with water clusters $(H_2O)_{1\leq n\leq 6}$ [1], hydrogen fluoride clusters $(HF)_{1\leq n\leq 4}$ [2], DNA bases and Watson-Crick base pairs [3,4], formamide and formic acid [5], amino acids [6], and ammonia clusters $(NH_3)_{1\leq n\leq 3}$ [7].

For a majority of the studied systems, their complexation occurs via the dominant ‘anchoring’ Au-Y (Y = F, O, N) bond at the edge of the Au_m cluster [8,9] where the gold cluster LUMO mostly protrudes. This anchoring is a necessary prerequisite to the formation of the nonconventional hydrogen bond. Under the anchoring formation, the Y atom of the interacting partner donates electron charge to the LUMO of the gold cluster, thereby inducing a through-bond charge transfer within the gold cluster. As a result, there appears excess negative charges on the unanchored-edge gold atoms that makes the corresponding lone-pair-like $5d_{\pm 2}$ and $6s$ orbitals available to the proton donor group of the interacting partner. The charge reorganization then results in a total flow of charge from the proton donor group to the acceptor gold atom, leading to the nonconventional X-H···Au hydrogen bonding. When the latter is formed, it donates backward to the anchoring one causing its reinforcement. It is also demonstrated that the gold-Y anchoring can activate the adjacent Y-H bond which in turn acquires all features inherent to the moderate/strong hydrogen bonds.

The anchoring and nonconventional H-bonding govern the DNA base and base pairs - gold interaction. The nature of the DNA – gold interaction predetermines and differentiates the affinity of the nucleobases (adenine, thymine, guanine, and cytosine) to gold. On the basis of detailed DFT computations, we provide the picture of the nucleobase – gold interaction patterns in terms of a large variety of features that cover the geometrical, energetic, spectroscopic, cluster-size, and gold coordination effects, the proton affinity and the deprotonation energy [3,4].The effect of the base - gold interaction on the Watson-Crick DNA pairing patterns is investigated in terms of the proton affinities and deprotonation energies of those proton acceptors and proton donors which are involved in the interbase hydrogen bondings. A variety of properties of the most stable Watson-Crick $[A\cdot T]$-Au_3 and $[G\cdot C]$-Au_3 hybridized complexes are described and compared with the isolated Watson-Crick $A\cdot T$ and $G\cdot C$ ones. It is shown that increasing the size of the gold cluster to Au_6 [3,4] results in a rather short gold-gold bond in the Watson-Crick interbase region of the $[G\cdot C]$-Au_6 complex that additionally bridges the $G\cdot C$ pair and thus ensures a significant strengthening of its pairing.

[1] E. S. Kryachko and F. Remacle, in Theoretical Aspects of Chemical Reactivity, A. Torro-Labbe (Ed.), Vol. 16 of Theoretical and Computational Chemistry, P. Politzer, (Ed.), Elsevier, Amsterdam, 2006. Ch. 11, pp. 219-250.

[2] E. S. Kryachko, A. Karpfen, and F. Remacle, *J. Phys. Chem.* **A 109** (2005) 7309.

[3] E. S. Kryachko and F. Remacle, *Nano Lett.* **5** (2005) 735.

[4] E. S. Kryachko and F. Remacle, *J. Phys. Chem.* **B 109** (2005) 0000.

[5] E. S. Kryachko and F. Remacle, *Chem. Phys. Lett.* **404** (2005) 142.

[6] E. S. Kryachko and F. Remacle, in Progress in Theoretical Chemistry and Physics, Vol. 15, J.-P. Julien, J. Maruani, D. Mayou, S. Wilson, and G. Delgado-Barrio (Eds.), Springer, Dordrecht, 2006. pp. 433-450.

[7] E. S. Kryachko and F. Remacle, in Progress in Theoretical Chemistry and Physics, Vol. 16, S. Lahmar, S. Wilson, and J. Maruani (Eds.), Springer, Dordrecht, 2007. pp. 175-210.

[8] F. Remacle and E. S. Kryachko, *Adv. Quantum Chemistry* **47** Ch. 23 (2004) 423-464.

[9] F. Remacle and E. S. Kryachko, *J. Chem. Phys.* **122** (2005) 044304.

Analysis of the biological activity of 1,4-benzodiazepine derivatives by means of HIT QSAR System

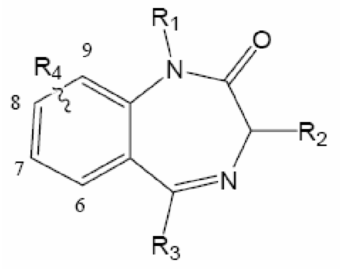
A.G. Artemenko[a], N.Ya. Golovenko[a], V.E. Kuz'min[a], E.N. Muratov[a,b],
D.V. Bondarover[c]

[a]*A.V.Bogatsky Physico-Chemical Institute of the National Academy of Sciences of Ukraine, 86 Lustdorfskaya doroga, Odessa 65080, Ukraine; E-mail: artanat@ukr.net*

[b]*Computational Center for Molecular Structure and Interactions, Jackson State University, Jackson, Mississippi, USA*

[c]*I. I. Mechnikov National University, Dvorianskaya 2, Odessa 65026, Ukraine*

Benzodiazepines (BDZs) are the drugs of choice in the pharmacotherapy of anxiety and related emotional disorders, sleep disorders, status epileptics, and other convulsive states; they are used as centrally acting muscles relaxants, for premedication, and as inducing agents in anesthesiology. They act via the benzodiazepine receptor site (BzR) on the γ-aminobutyric acid receptor ($GABA_A$) family and have been subjected to extensive quantitative structure-activity relationship (QSAR) studies.



The objective of the present work is QSAR analysis of biological activity of the 1,4-benzodiazepine derivatives by means of hierarchical informational QSAR technology (HIT) based on simplex representation of molecular structure (SiRMS)[1]. The main its advantages consists in follows: 1) Absence of "molecular alignment" problem; 2) Usage of molecular models with different adequacy degree; 3) Different physical and chemical properties of atoms taken into account; 4) The high adequacy and good interpretability of obtained models; 5) Clear ways for molecular design. This method allows providing rational selection of compounds with high specific biological activity.

The binding affinity (pIC_{50}) of ligands to benzodiazepine receptors ($GABA_A$/BzR) [2, 3] and oral bioavailability of compounds have been investigated. Completely adequate statistical partial least squares models have been obtained for all of the studied activities. On the base of the obtained QSAR models the molecular fragments both promoting and interfering the given biological activities have been determined. For example, is discovered that the presence of tert-butyl fragment (R_1), amino group (7-R_4) and 2-chloro-5-fluoro- benzene (R_3) promotes the binding affinity. The presence of substituents with high polarizability (7-R_4) has distinctly negative influence on binding affinity. The presence in the molecule of non-substituted benzene rings promotes its bioavailability and oxygen-containing fragments decreases ones.

Using the information about obtained statistical models the influence of different physico-chemical properties of investigated compounds on the changes of binding affinity and bioavailability was studied. These results specify the high role of hydrophobic factors in the both cases. The requirements to molecular design have been formulated.

[1] V.E. Kuz'min, A.G. Artemenko, P.G. Polischuk, E.N. Muratov, A.I. Khromov, Liahovskiy A.V., S.A. Andronati, S.Yu. Makan, *J. Mol. Mod.* **11** (2005) 457-467.

[2] D.J.Maddalena, G.A.R.Johnston, *J. Med. Chem.* **38** (1995) 715-724.

[3] J. J. Sutherland, L. A. O'Brien, D.F. Weaver, *J. Med. Chem.* **47** (2004) 5541-5554.

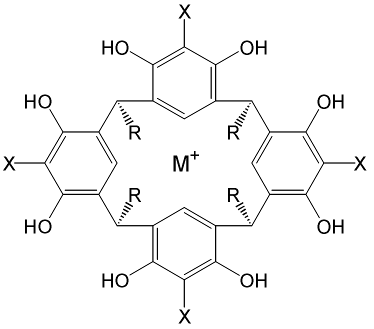
RI-DFT and RI-MP2 calculations in supramolecular chemistry: stabilities of host-guest complexes

A. B. Rozhenko[a,b], W.W. Schoeller[b], U. Manthe[b]

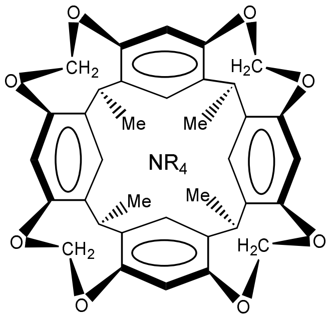
[a] Institute of Organic Chemistry of the National Academy of Sciences, Murmans'ka str. 5, 02094 Kyiv, Ukraine

[b] Fakultät für Chemie der Universität Bielefeld, Postfach 10 01 31, 33501 Bielefeld, Germany

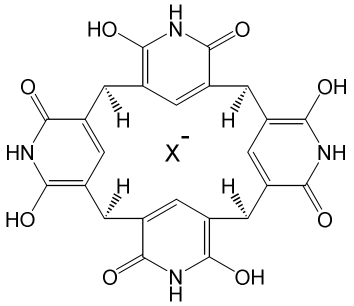
DFT calculations of stabilities of a number of the host-guest complexes have been performed with and without using of Resolution of the Identity (RI) algorithm. Complexes of calix[4]arenes **(1)** and cavitand **(2)** with alkali metal cations or with different ammonium cations was chosen as objects for investigation. In contrast to π-donor resorc[4]arenes, pyrogallo[4]arenes and structurally similar cavitands, pyridine[4]arene **(3)** is proven to build stable adducts with small anions. Such a different behavior inherent to these structurally similar classes of host molecules can be explained basing on their molecular orbitals. Pyridine[4]arene adducts exist in an equilibrium with the capsule structures **(4)**. The relative stabilities of the capsules in comparison with the corresponding monomers have been analyzed at the DFT (B3LYP and RI-BP86) level of approximation. The solvent effects have been taken into account using the COSMO model.



1

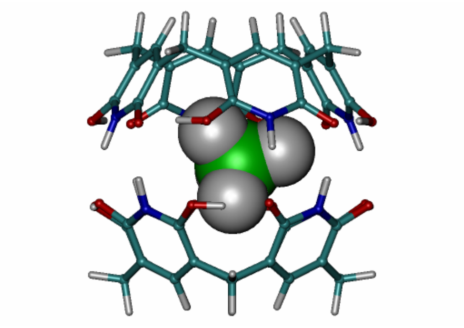


2



3

The calculated relative stabilities are compared with the ESI mass spectrometrical data.



4

The ordinary DFT methods describe poorly adducts built due to the van der Waals interactions. We present a first example of the structure optimization and calculation of vibration frequencies for the resorc[4]arene adduct with methyl iodide at the superior RI-MP2 level of approximation.

Rozhenko, A.B.; Schoeller, W.W.; Letzel, M.; Decker, B.; Agena, C.; Mattay, J. *J. Mol. Struct. (THEOCHEM)* **732** (2005) 7-20; Rozhenko, A.B.; Schoeller, W.W.; Letzel, M.; Decker, B.; Agena, C.; Mattay, J. *Chem., Eur. J.* **12** (2006) 8995-9000.

Electron and spin states of conjugated carbon

V. Khavryuchenko[a], O. Khavryuchenko[b], Yu. Tarasenko[a], V. Strelko[a]

[a]Institute for Sorption & Endoecology , National Academy of Sciences of Ukraine, Gen. Naumova str.13, 03680 Kiev, Ukraine; email: vkhavr@compchem.kiev.ua

[b]Kiev Taras Shevchenko National University, Chemical Faculty, Inorganic Chemistry Department, Volodymyrska str. 64, Kiev, Ukraine, e-mail: alexk@compchem.kiev.ua

Well known fact that scanning tunneling microscope (STM) image of graphite does not correspond its space structure for (0001) plane. Some explanations of this phenomenon were proposed, starting from the graphite interlayer interaction and layer packing up to very complicated models included relativistic effects. We have proposed simple model based on the usual quantum-chemical approach [1]. Experimental and quantum chemical investigation system shows that the basic (the most stable) electronic state of carbon materials with extensive conjugated is not simple singlet. Total spin density is not uniformly distributed over conjugated bond system, but spin alternation occurs. Depends on the structure, the most stable electronic state may be a singlet with spin alternation (flat graphite-like systems with terminated borders) or higher multiplicity states for non-classic aromatic systems (included azulen-like substructures) or non-trminated borders with twofold coordinated carbon atoms.

The carbon materials may consist of the two main domains: graphite-like and amorphous. The domains implicate the conjugated carbonic system consisting from 80 to 400 carbon atoms, and possess the non-zero total spin. The magnetic domains are separated by amorphous network, which may be formed by sp^3-hybridized carbon atoms or carben chains. The difference between energetic levels of different spin states of the carbon domain may be less than kT at ambient temperature. Therefore, the magnetic properties of the carbon materials are intrinsic and originate from the energetic stability of the high multiplicity states of the conjugated carbonic systems.

Doping of the carbon system by nitrogen and oxygen atoms may increase or decrease the stability of higher multiplicity states. But all studied systems (more 400 moleculs and clusters, which contains conjugated carbonic system at least 90 atoms) have ground state with lowest energy in singlet state with spin alternation or in higher multiplicity states.

The problem of ‘dangling bond’ is discussed in respect to the carbonization process, which is usually accompanied by dehydrogenation. The quantum chemical simulations show that the electronic density is distributed on the carbonic system upon the dehydrogenation. The elimination of hydrogen leads to the reconstruction of the carbonic backbone in order to decrease the system’s energy. Therefore, the ‘dangling bonds’ are not stable in the carbonized materials.

This concept, from our point of view, can explain a lot of chemical properties of carbon based materials, which quite differ from the properties of ordinary organic molecules with the same functional groups. There are the catalytic properties of active carbons in red-ox reactions, where carbon with its functional groups plays a role not only the electron transport media, but a proton transport intermediate, too.

Keywords: quantum chemistry simulation; amorphous and graphite-like carbons; electronic and spin states

[1] V.D.Khavryuchenko, Yu.A. Tarasenko, V.V. Strelko, O.V. Khavryuchenko, V.V.Lisnyak. "Quantum chemical study of polyaromatic hydrocarbons in high multiplisity states", *International Journal of Modern Physics* B, in press

Microscopic model of CO oxidation on Pt(111)

I.N. Yakovkin* and N.V. Petrova

Institute of Physics, National Academy of Sciences of Ukraine, Prospect Nauki 46, Kiev, 03028, Ukraine

A new microscopic model, based on DFT/LDA modeling, is suggested for the Langmuir-Hinshelwood reaction of catalytic CO oxidation in coadsorbed O-CO layers on Pt(111). We suggest also a new algorithm for realistic Monte Carlo simulations of associative desorption, which implements the microscopic description of the reaction with activation energy, found from DFT calculations. It has been found that only the oxygen atoms occupying threefold hollow sites of hcp type are chemically active. The potential barrier for the oxidation reaction significantly decreases due to changes in the adlayer oxygen states in the proximity to CO. The oxygen electronic density distribution is affected by approaching CO molecule which alters the oxygen position. Height of the barrier is estimated as 1.15 eV, which may be attributed to the upper limit of activation energy for the net reaction process.

Research Exchange Along the Modern Silk Road: From Electrons to Clinical Assays, China to Europe and Back

Gregory Chass

University of Wales / Beijing Normal University, School of Chemistry, U. Wales, Bangor, Wales, LL57 2UW

Over two millennia have passed since the Silk Roads channeled the flow of goods, people and information between the Orient and its Northern terminus in Krym. Both Europe and China benefited greatly from the exchange of knowledge in ancient times and again when the Polo family initiated its renaissance. The dawning of the 3rd millennium has need for another renaissance in the 'trade of knowledge' and mixing of culture, signaled by the current state of science and world economics.

Many modern scientific problems are multi-disciplinary in nature, thus such an exchange of knowledge is often required to formulating effective solutions. To err is to label knowledge as nothing other than information; it is instead defined as understanding, familiarity gained by experience and an organised body of information (a database).

The continued development of three established projects is essential to forging an effective knowledge trade along the modern Silk Road to solving modern problems in the molecular sciences (i.e. protein folding, drug side-effects, solvent effects)

Unified Computational Methodology

-a standardised, scalable, dynamic computational methodology of high efficacy

Computed Structure Database

-a central database to warehouse computed data and cross-reference with experiment

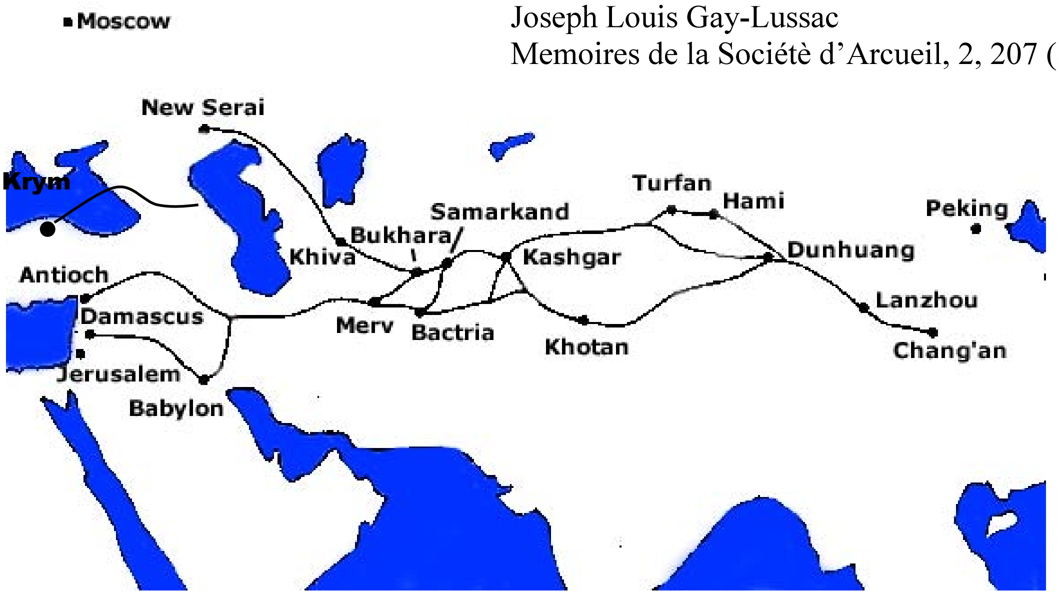
Standing Synergy Between Experiment and Theory

-'proof of concept' via a network of established experts and synergy between results

An academic path has already been established starting in Beijing, passing through Ukraine and Hungary, continuing through Italy, France and Spain, with a Western terminus in Wales. It is essential that a European investment be made into the people required to realise these projects and the European half of the Modern Silk Road.

"We are perhaps not far removed from the time when we shall be able to submit the bulk of chemical phenomena to calculation."

Joseph Louis Gay-Lussac
Memoires de la Sociétè d'Arcueil, 2, 207 (**1808**)



Elucidation of Solvent and Catalyst Effects Upon Activation Barriers by Means of the Reaction Force

Jane S. Murray[a], Jaroslav V. Burda[b], Alejandro Toro-Labbé[c],
Soledad Gutiérrez-Oliva[c], and Peter Politzer [a,c]

[a]Department of Chemistry, Cleveland State University, Cleveland, OH 44115, USA

[b]Department of Chemical Physics and Optics, Faculty of Mathematics and Physics, Charles University, Ke Karlovu 3, 112 16 Prague, Czech Republic

[c]Laboratorio de Química Teórica Computacional (QTC), Facultad de Química, Pontificia Universidad Católica de Chile, Vicuña Mackenna 4860, Casilla 306, Correo 22, Santiago, Chile

[d]Department of Chemistry, University of New Orleans, New Orleans, LA 70148, USA

The reaction force **F**(**R**) of a chemical or physical process is given by the negative derivative of the potential energy V(**R**) along an appropriate intrinsic reaction coordinate **R**. The maxima, minima and zeroes of **F**(**R**) divide the process, naturally and unambiguously, into well-defined stages. In particular, each activation barrier is found to be composed of two components, one of which reflects preparative structural factors while the other corresponds to the first part of the transition to products. By computing the magnitudes of these contributions both in the presence and absence of an external agent, such as a solvent or a catalyst, it is possible to determine whether the effect of that agent is primarily upon early structural changes or upon the transition state. Two examples will be discussed: (a) the effects of aqueous solution upon an S_N2 reaction, and (b) the role of Mg^{++} in catalyzing the tautomerization of thymine.

Quantum chemical simulation of the relaxation and thermally stimulated processes: a vibration excitation-relaxation stochastic optimization

Volodymyr D. Khavryutchenko[a], Oleksiy V. Khavryuchenko[b] and Vladyslav V. Lisnyak[b]

[a] ***Institute for Sorption and Problems of Endoecology, National Academy of Sciences of Ukraine, Gen. Naumova Street 13, Kiev 03680, Ukraine***

[b] ***Chemical Department, Kiev National Taras Shevchenko University, Vladimirskaya Street. 64, Kiev 01033, Ukraine***

A new method for the theoretical examination of thermal inter-conversions via the space structure vibration excitation-relaxation stochastic (VERS) optimization method has been proposed. The original software to perform implementation of the methodology has been developed and tested on silica 27 SiO_2 cluster. A set of thermodynamically probable space structures of amorphous silica particles and temperatures of their inter-conversions have been quantum chemically simulated. Finally, the simulated space structures have been verified by the comparison of calculated inelastic neutron scattering spectra of different highly dispersed silicas with experimental ones. The clusters obtained on different stages of heating can reproduce the relative volume, the coordination numbers distribution and the INS spectra of real objects e.g. the fumed silica, the silica fume and the silica glass.

Energy components alternation method for conformational search of flexible atomic chains

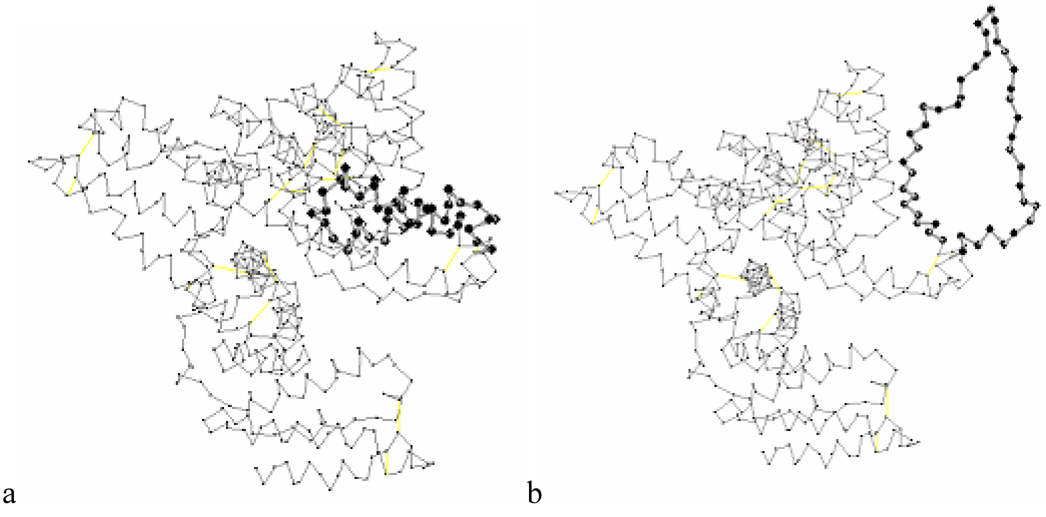
I.E. Shchechkin, T.O. Hushcha

Institute of Bioorganic Chemistry and Petrochemistry, National Academy of Science of Ukraine, 1 Murmanska str., 02660, Kyiv-94, Ukraine, e-mail: shch406@bpci.kiev.ua

The algorithm is proposed to search conformational space of long flexible polypeptide chains. Its principal feature is that potential energy function is partitioned; the components are handled separately, taking into account each component peculiarity. Series of geometry optimization runs by a gradient-based method is performed using scoring function, where some of the components are weakened in every run. So if a potential energy function is represented as the sum $P = \sum p_i$, then the scoring function is $S = \sum k_i p_i$, where p_i are some components of the potential function, and $0 \le k_i \le 1$ are the weakening factors. Partitioning of the potential function may be done in many different ways, and the factors k_i can be varied as a subsequent run of the series shifts the foregoing one. There are two extreme cases here: one of them is when all except single k_i factors equal to 0, and the other one occurs when all k_i equal to 1. The first case corresponds to a search-character procedure (provided that in every successive run the nonzero factor is different), and the second one conforms to the plain local minimization of the whole potential function. Gradual drift according to certain schedule from the first case to the second one implies performing of a global minimization.

An instance of such an approach to a wide-range conformational search has been implemented in our *FlexiChain* software. Full potential was represented by the sum of the most valuable pairwise atom-atom terms with all except one factors being zero and the nonzero factor possessing the value of 1.0. In other words, only single pairwise atom-atom potential term was taken into account in every minimization run. The term, which will be nonzero, is randomly chosen. To make evaluation faster the real potential terms were substituted with simplified models, which mimic the principal features of the real terms. Gradient-based minimizer (Fletcher-Davidon-Powell) was combined with Gelfand-Tsetlin ravine algorithm, which appeared to gain better minimization.

This algorithm was employed for conformational search in dihedral angle space of the loop-like 125-167 fragment of human serum albumin (HSA) while treating the rest of the molecule as a single rigid structure. Several stable conformers of the fragment that considerably differ in 3D-structure from the original one were obtained. Some of the new found conformers do not have any major attractive nonbonded contacts with the protein globule, and some of them form hydrogen bonds with the neighbor domains of the molecule. The latter enables to suppose that conformational transition of the 125-167 fragment affects domain mutual mobility.



a b

Native (a) and new found (b) conformations of 125-167 loop-like fragment (bold) of HSA

Extrapolation techniques for determination of the relative energies of conformers and barriers to conformational transitions

V.A. Bataev, S.I. Bokarev, O.S. Bokareva, E.V. Rastoltseva, I.A. Godunov

Chemistry Department Moscow State University, 119992, Moscow, Russia
E-mail: lant@phys.chem.msu.ru

Extrapolative VFPA (Valence Focal-Point Analysis) technique [see e.g. A.G. Császár, W.D. Allen, H.F. Shaefer III, J. Chem. Phys. (1998) V. 108, P. 9751] is based on a series of quantum-chemical methods with a successive increase of account for electron correlation (in the present work: HF→MP2→MP3→MP4→… and HF→MP2→CCSD→CCSD(T) →…) and on series of correlation-consistent basis sets (aug)-cc-p(C)XZ (X=D,T,Q,5,6). Such approach allows performing two-dimensional (method/basis) extrapolation to the Full Configuration Interaction method within a Complete Basis Set. Obtained values are corrected for zero point vibrational energy, relativistic corrections, core-valence correlation, and non-Born-Oppenheimer effects.

This scheme was applied to precisely estimate relative energies of conformers and barriers to internal rotation of aliphatic (CH_3CFO, CH_3CClO, CH_3CH_2CHO, and $(CH_3)_2CHCHO$), α,β-unsaturated ($CH_2=CHCHO$), and cyclopropane ring containing (C_3H_5CHO) carbonyl molecules in the ground state. Utilization of VFPA-technique for estimations of barriers of conformational transitions of formaldehyde and its halogen derivatives (CXYO (X=H, F, Cl)) and other carbonyl molecules (CH_3CFO, CH_3CClO, CH_3CH_2CHO) in the lowest triplet excited electronic state is also discussed.

Results were compared with experimental data as well as with estimations of other high-level (QCISD и CCSD(T)) quantum-chemical methods and the results of “semi-empirical” approaches based on *ab initio* and (or) DFT calculations designed for evaluation of thermodynamic parameters (G2, G3 and their modifications).

This work is financially supported by the Russian Foundation for Basic Research (grant N 07-03-00090).

Potential energy curves and atomization energies from density functional theory with a local parameterized potential

S.I. Fesenko, V.N. Glushkov

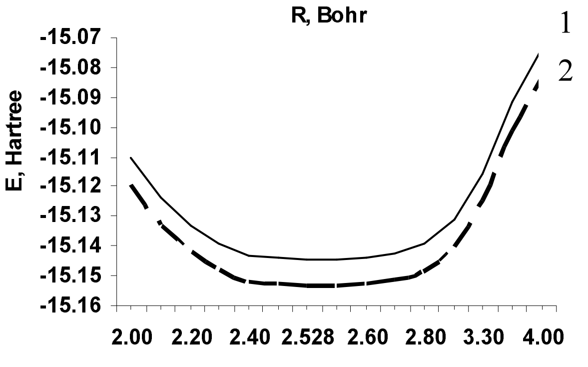
Dept. of Physics, Dnepropetrovsk National University, Ukraine

A direct-mapping density functional theory (DM-DFT) has been recently proposed [1,2] where an effective potential, V_{eff} (**r**), is expressed in terms of the external potential, i.e. the electron-nucleus interaction potential in a case of atoms and molecules. Unlike the traditional implementation of DFT, where the potential is an explicit or implicit functional of the electronic density this method deals with V_{eff} (**r**) as a functional of the external potential. In Ref.[3] we have been introduced the two-parametric form of V_{eff} (**r**; C, β) :

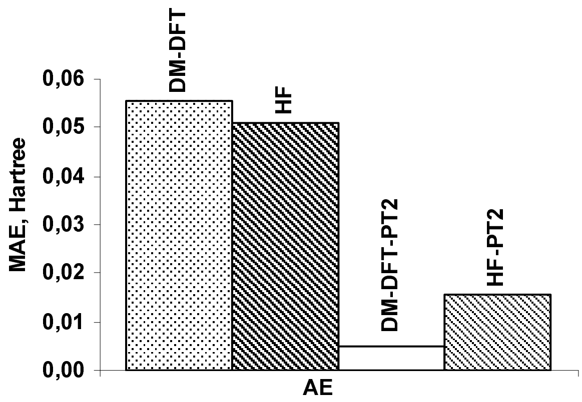
$$V_{eff}(\mathbf{r}) = -\sum_k \frac{Z_k}{|R_k - r|} + \frac{N-1}{Z} C \left\{ \sum_k \frac{Z_k}{|R_k - r|} [(1 - \exp(-Z_k^{\beta}|r-R_k|))] \right\} \qquad (1)$$

The equations for optimization of the parameters C and β have been derived using the exchange-only approximation and the preliminary tests of DM-DFT method with the effective potential (1) have been reported. In particular, the total energies of the molecules calculated with the exchange-only potential were found to deviate slightly from the exact Hartree-Fock ones.

In this presentation we further develop and apply the DM-DFT method to calculations of the potential energy curves and atomization energies (AE) of molecules.



Energy as a function of **R** for BeH :
1 – DM-DFT; 2 – HF.



Mean absolute error in atomization energies (AE) computed by different methods

The potential energy curves calculated with the exchange-only approximation and the total atomization energies computed with the second-order perturbation theory (PT2) were found to be in agreement with benchmark results obtained with *ab initio* wave mechanics methods.

[1] Theophilou A.K. in: The fundamentals of Electron Density, Density Matrix and Density Functional Theory in Atoms, Molecules and Solids State. Ed. By N.I.Gidopoulos and S.Wilson (Kluwer, 2003).
[2] Theophilou A.K. , Papaconstantinou P.G. and Glushkov .V.N., *J.Phys. Conf. Ser.* **30** (2006) 249.
[3] Glushkov V.N., S.I.Fesenko, *J.Chem.Phys.* **125** (2006) 234111.

Modified 6-31G$^{\#\#}$ basis set in DFT calculations of NMR spin-spin coupling constants

Vladimir I. Bolshakov[a], Vladimir V. Rossikhin[a], Eugene O. Voronkov[b],
Sergiy I. Okovytyy[c,d], and Jerzy Leszczynski[d]

[a]Pridneprovs'ka State Academy of Civil Engineering and Architecture, 49635, Ukraine,

[b]Dnepropetrovsk National Technical University, Dnepropetrovsk, 49010, Ukraine,
[c]Dnepropetrovsk National University, Dnepropetrovsk, 49050, Ukraine,

[d]Computational Center for Molecular Structure and Interactions, Department of Chemistry, Jackson State University, Jackson, Mississippi 39217

Recently we have proposed [1] and then tested (e.g. [2, 3]) magnetically corrected 6-31G$^{\#\#}$ basis set constructed by augmentation of standard 6-31G basis set by functions, obtained from solution of the nonhomogeneous Schrödinger equation for the model problem "one-electron atom in an external uniform magnetic field" using the closed representation of the Green's function. It should be noted that addition functions have been obtained from the response functions, which take into account the influence of both valence and core orbitals.

In this report, we present the results that were obtained to investigate the performance of magnetically corrected 6-31G$^{\#\#}$ basis set for calculations of indirect spin-spin coupling constants at DFT level of theory. The series of compounds chosen for this study includes hydrides (HF, HCl, HBr, H_2O, NH_3, CH_4, PH_3, AsH_3, GeH_4), homo- and heteronuclear dihalogens (F_2, Cl_2, Br_2, FBr), molecules with double and triple bonds (CO, N_2,,HCN), and Fe- Mn- Ni- cenes.

Calculations performed using Gaussian 03 program [4] using pure (BP86) and hybrid (BLYP, BLYP(50,50), B3LYP, PBE1PBE) density functionals. The 6-31G$^{\#\#}$ basis set has been used in two variations – first as described in [1] and second with decontracting of S-functions from initial standard basis set and addition p-functions or with decontracting d-, f-functions from proposed one for more accurate correction of Fermi-contact or paramagnetic spin-orbit terms, correspondingly. Geometrical parameters have been preliminary optimized in frame of the same levels of theory.

It is shown that for molecules with dominant contribution of Fermi-contact term improvement of calculation's accuracy is achieved by simultaneous decontracting of basic S-functions and induced by them additional p-functions.

For accurate description of paramagnetic spin-orbit contribution we have used decontracting of additional d- and f- basis functions. In comparison with experimental data overestimate results for molecules with multi-bonds in uncontracted 6-31G$^{\#\#}$ basis is corrected by decontraction of additional p-functions only. It should be noted, that decontraction practically does not change value of proton spin-spin coupling constant, however essentially reduces values of Fermi-contact terms for non-hydrogen spin-spin coupling constants.

[1] Rossikhin V.V., Kuz'menko V.V., Voronkov E.O., Zaslavskaya L.I. *J. Phys. Chem.* **100**(51) (1996) 19801.
[2] Okovytyy S.I., Rossikhin V.V., Voronkov E.O., Leszczynski J. *J. Phys. Chem.* A **108**(27) (2004) 4030.
[3] Bolshakov V.I., Rossikhin V.V., Voronkov E.O., Okovytyy S.I., Leszczynski J. *J. Comp. Chem.* **28**(4) (2007) 778.
[4] M. J. Frisch, G. W. Trucks, H. B. Schlegel, et al., *Gaussian, Inc.*, Wallingford CT, 2004.

Spectroscopic parameters of diatomic molecules in the Complete Active Space Coupled Cluster Theory

Dmitry I. Lyakh, Tatiana A. Klimenko and Vladimir V. Ivanov

V. N. Karazin Kharkiv National University, E-mail: <vivanov@univer.kharkov.ua>

Very precise calculations of spectroscopic properties of small molecules (in different electronic states) usually encounter three general problems. The first is connected with an accurate calculation of separate points of the potential energy surface (PES) providing that the adiabatic approximation is used. The second problem is to obtain an accurate approximation of the PES using an analytical function. The third problem is calculation of rotational–vibronic states (and parameters) by solving the Schrodinger equation and corresponding series of perturbation theory equations. In this talk we present the results of our calculations with the use of the state specific multireference coupled cluster singles and doubles approach with the complete active space reference (CASCCSD). The wave function in the CASCCSD has in general the following form:

$$\left|\Psi_{\mathrm{CASCCSD}}\right\rangle = \exp\left(T_1^{(\mathrm{ext})} + T_2^{(\mathrm{ext})}\right)\left(1 + C^{(\mathrm{int})}\right)\left|0\right\rangle, \qquad (1)$$

where the operator $T^{(\mathrm{ext})}$ generates all single and double excited determinants from all reference functions which are generated by the operator $\left(1 + C^{(\mathrm{int})}\right)$. All above functions can be expressed as different order excitations from the so called *formal reference* determinant ($\left|0\right\rangle$). Such a form of the coupled cluster *ansatz* has demonstrated perfect description of PES in difficult quasi-degenerate cases. For an adequate approximation of the PES obtained with (1) we used a potential in a form of *generalized Morse function*:

$$V(r) = \sum_{m=2}^{q} \alpha_m \left(1 - \exp^{-\beta_m (r - r_e)}\right)^m, \qquad (2)$$

where an internuclear separation and equilibrium distance are r and r_e respectively. Parameters α_m and β_m are fitted by the non-linear least squares method. Our calculations showed that $q = 3 - 5$ are enough for precise description of PES between separate points. The pure vibrational radial Schrodinger equation with the potential (2) was solved by using a new approach based on the Numerov's method. The energies of different vibrational states, G_v, were compared with experimental values and other theoretical data. When rotational effects are not neglected the effective potential (2) becomes:

$$V(r) + J(J+1)/2\mu r^2, \qquad (3)$$

where the rotational quantum number is J and μ is a reduced mass of the nuclei. A set of rotational (B_v) and centrifugal distortion ($D_v, H_v, L_v, \ldots$) parameters was calculated using the perturbation theory:

$$B_v = \left\langle \varphi_v^{(0)} \middle| 1/r^2 \middle| \varphi_v^{(0)} \right\rangle; \quad D_v = -\left\langle \varphi_v^{(1)} \middle| 1/r^2 \middle| \varphi_v^{(0)} \right\rangle; \quad H_v = -\left\langle \varphi_v^{(1)} \middle| 1/r^2 - B_v \middle| \varphi_v^{(1)} \right\rangle, \ \textit{etc.}, \qquad (4)$$

where the $\varphi_v^{(1)}$ is the first order correction to the unperturbed vibrational wave function $\varphi_v^{(0)}$:

$$\varphi_v^{(1)\prime\prime} + 2\mu\left(G_v - V(r)\right)\varphi_v^{(1)} = -2\mu\left(B_v - \frac{1}{r^2}\right)\varphi_v^{(0)} \qquad (5)$$

Significant problem is a numerical calculation of the above parameters at higher vibrational levels. The nuclear motion wave function and corresponding corrections for such levels are essentially alternating in sign. New approach based on *Galerkin projection scheme* for the equations like (5) has demonstrated high numerical stability.

The second-order Kohn-Sham perturbation theory for excited states

V.N. Glushkov

Dept. of Physics, Dnepropetrovsk National University, Ukraine

In the course of the development of density functional theory (DFT), distinct levels of approximation for the exchange-correlation potentials, $V_{xc}(\mathbf{r})$, can be identified. Recently, there has been an enormous development in the construction of a new generation of $V_{xc}(\mathbf{r})$ expressed explicitly in terms of the Kohn-Sham (KS) orbitals. Exchange can be calculated exactly via the optimized effective potential (OEP) method. A promising prescription for obtaining a correlation potential that performs well with the OEP exchange is based on many-body perturbation theory using the KS determinant as a reference. This state-of-the-art theory is capable of giving good accuracy in calculating the ground state properties.

There are several possible approaches for generalization of DFT to excited states (ESs). However, at present, there are scarce DFT calculations for ESs based on the above methodology. We have recently proposed the amended KS equations and an alternative OEP approach to the ES problem [1,2]. It was based on DFT for individual ESs and a simple to implement method which takes the orthogonality constraint into account [3]. The KS excited determinants are orthogonal to the determinants for states of lower energies. Preliminary exchange-only calculations carried out for some atoms and molecules were encouraging. The total ES energies calculated had their relative deviations ($\Delta E/E$) from the Hartree-Fock ones of the order of 10^{-4}.

In this communication we further develop DFT for individual ESs. In addition to Refs. [1,2], orbital-dependent correlation functional for ESs is derived from the many-body perturbation theory based on the Kohn-Sham orbitals and orbital energies. The total ES energies of the simple diatomics computed with the second-order such a theory were found to be in agreement with benchmark results obtained with configuration interaction methods.

[1] Glushkov .V.N., *Opt&Spectrosc.* **99** (2005) 684.
[2] Glushkov .V.N. , Levy M., *J.Chem.Phys.* 2007 (to be published)
[3] Glushkov V.N., *J.Math.Chem.* **31** (2002) 91 ; *Opt&Spectrosc.* **93** (2002) 11

FastNMR: A High Performance NMR Simulation Tool

V.F. Galat[a]

[a] ***Institute for Physical Organic and Coal Chemistry, R.Luxemburg str. 70, 83114 Donetsk, Ukraine, email: v_galat@rambler.ru***

Despite of development of computer technologies, and constantly growing power and speed of personal computers, the designing of fast and performance algorithms still will be long to remain actual, as, on the one hand, progress of computer engineering stimulates scientific modeling to research of more and more complex systems, and on the other hand, the modeling of such systems requires the increasing computer resources and speed of processors. The Nuclear Magnetic Resonance (NMR) as an analytical method of study of molecules in their natural environment is unique, as from the point of view, volume, ease and completeness of the received information, and from the point of view of abilities of modeling of experiment results. NMR theory, is extremely well developed for the last 50 years, gives exclusive abilities of modeling of NMR-experiments practically to any complexity. At the same time level of development of the appropriate software, which would use modern achievement both NMR theory, and computer technologies, is much lower. In spite of the fact that there is a set of the numerical solutions of problems of modeling in NMR, all of them are not accomplished. One of them execute too slowly, others are extremely difficult for practical use and adaptation. Now two UNIX-packages *GAMMA*[1] and *BlochLib* [2] are known only for us, which would cover the most complete set of NMR-modeling problems. But use them under Windows environment, which is dominant in the Europe countries, is impossible without essential revising of an initial code.

In the given paper we represent a Windows-package *fastNMR*, designed for quantum mechanical modeling of high resolution NMR problems practically of any type and complexity. The choice as the basic programming language – *OOP Pascal* - is caused by its high popularity in the countries of East Europe, simplicity of syntax and ease of perception of an initial code. Despite of it, by the opportunities he a little, in what concedes to language C ++ (most popular programming language in the countries of Northern America), and the executed code, generated by the modern Pascal-compiler, works only on 10-20 % more slowly, than appropriate C++ code. Last gap can be easily corrected by replacement of the most time-consuming parts of a code by an assembler code. The initial code of a package is optimized under the most widespread types of processors - Pentium, AMD and Celeron, and shows high speed of calculations. Comparison with the accessible trial versions of the popular NMR programs *MestReC* [3], *gNMR* [4] and *PERCH* [5] demonstrates higher speed of calculations *fastNMR* in comparison with *MestReC* in 100 times, more than in 10 times in comparison with *gNMR*, and in 5 times is faster, than *PERCH*. Utilizing modern numerical methods and algorithms allows study of complex molecular systems, such as biomolecules etc. Relaxation and chemical exchange using Liouville space operators are also included. The presence of the graphic interface essentially simplifies use of a package by the users. High performance algorithms designed in the *fastNMR* can be used not only in NMR-modeling, but also in many other areas of computing chemistry and physics.

[1] S. Smith, T. Levante, B. Meier, R. Ernst, J. Magn. Reson. 106a (1994) 75.
[2] W.B. Blanton, J. Magn. Reson. 162 (2003) 269.
[3] http://www.mestrec.com/
[4] http://www.adeptscience.co.uk/products/lab/gnmr/
[5] http://www.perchsolutions.com/

GPU4DFT – powerful accelerator for Ab initio calculations on ordinary personal computer

A.V. Semanin

Department of cybernetics and computer engineering, Sevastopol State Technical University, Sevastopol, 99053 Ukraine.

The fast growing videogame industry exerts strong economic pressure that forces constant innovation in developing of graphics processor units (GPU). The GPU has evolved into a very flexible and powerful coprocessor with a lot of Gflops/sec and just now even Tflops/sec. It has own large memory with high bandwidth and low latency. Architecture of GPU differs from classical von Neumann's machine and this is the reason why the traditional algorithm could not be executed on this GPU. However, it's possible to create the programs that simulate the execution of standard programs and carries out on GPU.

The author propose gpu4dft program that realize the above method for some parts of the standard libraries such as FFTW, BLAS, LAPACK, CLAPACK, ATLAS that are extensively used in Ab initio molecular dynamics simulations. Using this technique we have been able to achieve performance on ATI Radeon 1950XTX 120 Gflops/sec for dense matrix multiplication and on NVIDIA GeForce 8800GTX 50 FFTbench Gflops/sec for 1D complex FFT. For comparison, ATLAS has demonstrated only 4 Gflops/sec for matrix multiplication on 1.5 GHz Pentium 4 using Intel's SSE2 SIMD instruction [1].There NVIDIA GeForce 8800GTX in one computer outruns approximately 300 central processing units (CPU) in cluster of workstation. To provide maximum flexibility usage gpu4dft program contains the Fortran interface in the form of wrapper functions. Gpu4dft program is written in C with application of Close to The Metal (CTM) API for ATI Radeon GPU and Compute Unified Device Architecture (CUDA) API for NVIDIA GPU correspondently. The execution environment is windows and linux.

Usually three calculation parts in the DFT calculation are mainly time-consuming: the evaluation of Hamiltonian matrix elements, the solution of Poisson's equation, and the diagonalization of the generalized secular equation. The gpu4dft program attained computational effects for every of each calculation parts. It can be used with most widely extended programs for DFT calculation e.g. Octopus, OpenMX, CPMD. Greater effect could be achieved by means of creation of special methods of computational chemistry for direct execution on GPU. Cooperation in this field of research is highly appreciated.

As GPU growth continues to outpace CPU growth, the author expects the GPU will become the preferred platform for high-performance scientific computing.

[1] Dongarra, J. 2001. An update of a couple of tools: ATLAS and PAPI. DOE Salishan Meeting (available from www.netlib.org/utk/people/JackDongarra/SLIDES/salishan.ps).

Quantum Chemical Study of Aromaticity of Six-Membered Monoheterocycles

Irina V. Omelchenko, Roman I. Zubatyuk, Oleg V. Shishkin

STC "Institute for Single Crystals", National Academy of Science of Ukraine, 60 Lenina ave., Kharkiv 61001, Ukraine

E-mail: irina@xray.isc.kharkov.com

The way of the quantitative determination of aromaticity is one of the most controversial issues relating to the aromaticity concept. The question about the possibility of aromaticity description by a single property of the molecule was raised repeatedly during last decade.

Aromaticity of the set of six-membered monoheterocycles (C_5H_5X: X=CH, SiH, GeH, N, P, As, O^+, S^+, Se^+) was studied at the MP2/cc-pVTZ level of theory using structural (Bird index I_6), energetic (ASE), magnetic (NICS(1)*zz*), and structural-dynamic (out-of-plane deformation force constant, kE) aromaticity indices. It was found that all of the molecules are highly aromatic. All used indices provide qualitatively correct description of aromaticity change with increase of atomic number of heteroatom, except for pyrillium cation. For this cation a low aromaticity was indicated by all indices excepting kE. This was explained by high electronegativity of the oxygen atom resulting in low contribution of classic Kekule resonance structures and substantial σ-character of the $C\text{-}O^+$ bond.

As for quantitative comparison, good correlations were found only for the pairs of indices I_6-NICS(1)*zz* and ASE-kE. Almost no correlation is observed between these two groups of indices. This fact reveals that the aromaticity of six-membered heterocycles can be described by at least two independent properties of the molecules.

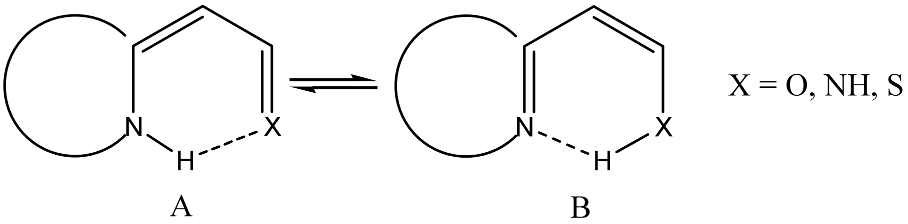
Influence of Exocyclic Proton Donor/Acceptor on Tautomerism, Aromaticity and Intramolecular Resonance-Assisted Hydrogen Bonds

Roman I. Zubatyuk, Oleg V. Shishkin

STC "Institute for Single Crystals" National Academy Science of Ukraine, 60 Lenina ave., Kharkov, 61001 , Ukraine

E-mail: roman@xray.isc.kharkov.com

Hydrogen bonding, aromaticity and tautomerism occupy a prominent position in heterocyclic chemistry. They significantly influence the structure, relative stability of tautomers (or isomers), reactivity and character of intramolecular interactions of various organic molecules. One of the most interesting topics is the relationship between aromaticity of the heterocycle, position of tautomeric equilibrium, and strength of intramolecular hydrogen bonds.



The tautomers of the set of molecules containing different types of heterocycles were studied with ab initio quantum-chemical methods at the MP2/AUG-cc-pVDZ level of theory. It was demonstrated that the relative stability of tautomers is controlled mainly by the two factors: relative inherent proton affinity of heteroatoms involved into hydrogen bond, and the change of heterocycle aromaticity in two tautomers. The influence of the substituent on the aromaticity of heterocycle is provided due to the different π-donating/accepting properties of heteroatoms leading to the change of π-charge on the heterocycle.

It was revealed that the hydrogen bonds in these molecules are resonance assisted. Their strength depends on the efficiency of resonance in the spacer, which in turn is controlled by π-donating/accepting properties of heterocycle and substituent. The mechanism of interplay between heterocycle aromaticity, intermolecular hydrogen bond strength and spacer polarization was revealed.

Analysis of intramolecular hydrogen bonds of actinocin derivatives - analogues of the anticancer antibiotics

O.S. Sukhanov, A.V. Shestopalova, K.V. Miroshnychenko

Department of Biological Physics, Institute of Radiophysics and Electronics, National Academy of Sciences of Ukraine, Kharkiv, 61085, Acad. Proskura Str.12, Ukraine

The aim of the research work was to investigate the structure and the properties of conformers of actinocine derivatives with different length of side chains: double protonated actinocin bis(2-dimethylaminoethyl)amide (ActII^{2+}), actinocin bis(2-dimethylamino-propyl)amide (ActIII^{2+}) and actinocin bis(2-dimethylaminobutil)amide (ActIV^{2+}) (Fig.1). These actinocin derivatives are the analogues of anticancer antibiotic Actinomycin D. They interact with DNA molecules by intercalation or minor groove type of binding [1]. It is also known that they can exist in solution as an equilibrium mixture of several conformations with different number of intramolecular hydrogen bonds [2].

In order to improve our understanding of existence of multiple conformations of actinocin derivatives, we carried out geometry optimizations, harmonic vibrational frequencies and molecular thermodynamic characteristic calculations with density functional method at B3LYP/6-31G* level of theory. Also our particular interest consists in the investigation of influence of intramolecular hydrogen bonds on the relative energies, geometric parameters and charges of actinocin derivatives. A Bader's atoms-in-molecules (AIM) topological analysis of the election density distribution was used for the study of characteristics of hydrogen bonds.

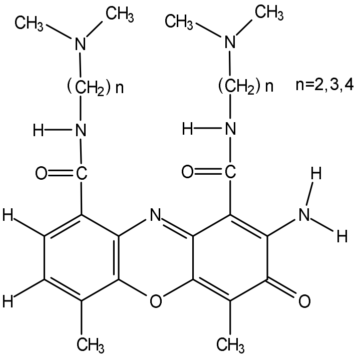


Fig. 1. Actinocin derivatives: n =2 - actinocin bis(2-dimethylaminoethyl)amide (ActII^{2+}), n =3 - actinocin bis(2-dimethylaminopropyl)amide (ActIII^{2+}), n=4 - actinocin bis(2-dimethylaminobutil)amide (ActIV^{2+}).

It was found that double protonated molecules ActII^{2+}, ActIII^{2+}, ActIV^{2+} are characterized by extended net of intramolecular hydrogen bonds. The properties and quantity of hydrogen bonds play essential role in the conformer stabilization. The results of the calculations and their analysis demonstrated that the relative energies (ΔE) were changed up to 17 kcal/mol, 18 kcal/mol and 15 kcal/mol during conformational transitions for ActII^{2+}, ActIII^{2+}, ActIV^{2+}, respectively.

For actinocin derivative ActIII^{2+} the some different tautomers were obtained and the influence of chlorine ion (Cl$^-$) on the formation of intramolecular hydrogen bonds was analyzed. *Ab initio* calculations revealed small probability of tautomer transition in the system ActIII^{2+} since the difference in the Gibbs free energies could amount to 27 kcal/mol. It was shown that the position of Cl$^-$ is essential for conformer relative energies and charges of atoms due to the additional polarization of ActIII^{2+} molecules. According to the results of calculation in PCM approach water dramatically influences on the relative energies of tautomeric forms of ActIII^{2+}. It was shown that in the water environment ActIII^{2+} possess much more conformational lability.

[1] V.Ya. Maleev, M.A. Semenov, E.B. Kruglova, T.V. Bolbukh, A.I. Gasan, E.G. Bereznyak, A.V. Shestopalova, *J. Mol. Struct.* **645** (2003) 145.

[2] V.S. Sibirtsev, E.N. Glibin, S.D. Ivanov, *Russian J.Org.Chem.* **36** (2000) 1812.

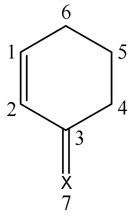
Structure and ring inversion of derivatives of cyclohexene with exocyclic double bond

S.V. Shishkina, S.M. Desenko, O.V. Shishkin

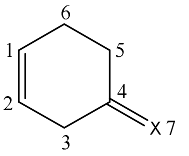
STC "Institute for Single Crystals", National Academy of Science of Ukraine, 60 Lenina ave., Kharkiv 61001, Ukraine, E-mail: sveta@xray.isc.kharkov.com

Recently [1] it was demonstrated that the ring inversion process in cyclohexene has unusual character. It includes three stages. The first stage is the transformation of the equilibrium half-chair conformation into a twist-boat via the sofa conformation with 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 change in energy of molecule. The third stage involves the transition from a twist-boat to a half-chair conformation accompanied by a significant decrease in energy. Later [2] it was demonstrated that 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. The loss of symmetry leads to the change of the character of the ring inversion process.

Other way to break the symmetry of the cyclohexene molecule is the replacement of one of the methylene groups by the exocyclic double bond. Therefore, we performed the systematic investigation of the equilibrium geometry, ring interconversion barrier and pathway for the molecules **1-12** at the MP2/6-311G(d) level of theory.



1 X=O
2 X=NH
3 X=S
4 X=PH
5 X=Se
6 X=AsH



7 X=O
8 X=NH
9 X=S
10 X=PH
11 X=Se
12 X=AsH

Results of calculation demonstrate that the equilibrium conformation of the molecules **1-12** is an asymmetrical half-chair. The value of the barrier for ring inversion does not depend from the nature of heteroatom. The most interesting results concern to the interaction of the exocyclic and endocyclic double bonds. One can assume that the exocyclic double bond in non-conjugated position with C=C bond influence on the symmetry of the ring noticeably smaller. The potential energy profile of the ring inversion for molecules **7-12** is very similar to one in cyclohexene. This indicates that exocyclic double bond perturbs intramolecular interactions in cyclohexene to a significantly smaller extent as compared to heteroatom.

[1] S.V.Shishkina, O.V.Shishkin, J.Leszczynski, *Chem.Phys.Lett.*, **354**(5-6) (2002) 428-434.
[2] S.V.Shishkina, O.V.Shishkin, S.M.Desenko, J.Leszczynki, *J.Phys.Chem.* A **111** (2007) 2368-2376.

An *ab initio* Study of Tautomeric Isomerism of Gossypol

A.F. Dmitruk, V.I. Rybachenko, C.Yu. Chotii, N.S. Ilkevych, O.M. Zarechnaya

L.M. Litvinenko Institute of Physical Organic and Coal Chemistry NASU (dmitruk@kaf.donduet.edu.ua)

Gossypol 1,1′,6,6′,7,7′-hexahydroxy- 5,5′ - diisopropyl – 3,3′- dimethyl - 2,2′ - binaphthalene – 8,8′ - dicarboxaldehyde is a plant biologically active substance from cotton, which determines its toxicity. According to IR and ^{1}H NMR studies it was found [1] that in different solvents gossypol occurs in three different tautomeric structures (Fig. 1 presents tautomeric structures of gossypol and atom numeration of its molecule).

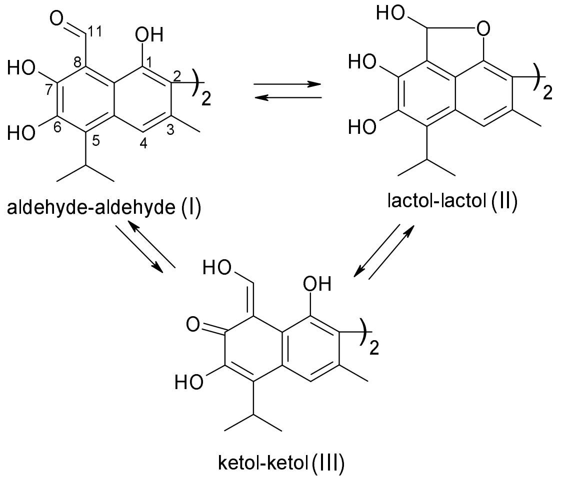


Fig.1. Tautomeric structures of gossypol [2].

Table. Ratio (%) of aldehyde (I), lactol (II) and ketol (III) forms in tautomeric equilibrium of gossypol

Analysis		Tautomer		
		I	II	III
PM3, vacuum		5	95	~ 0
ab initio	vacuum	100	~ 0	~ 0
	DMSO	11 (17)*	89 (83)*	~ 0 (0)*
	chloroform	96 (100)*	4 (0)*	~ 0 (0)*

* - estimation according to experimental data [2]

In this communication results of quantum-chemical investigation of gossypol tautomeric equilibrium in vacuum and in solution of DMSO and chloroform have been discussed. *Ab initio* calculations were carried out in 6-31G basis set using program GAMESS [1]. Effect of solvent was taken into account with the help of continual model PCM.

According to PM3 semiempirical approximation in all tautomers naphthalene rings are practically orthogonal (dihedral angle 322′3′ for I and III is close to 90°, while for II it is about 80°). *Ab initio* calculations give the value of this angle somewhat smaller. Thus, this angle for I и III is about 80°, while for II - 60°. In *ab initio* calculations bond length 2-2′ is 0.02Å longer than in PM3 approximation and equals 1.50Å for I and III, while for II – 1.49Å. It is necessary to note that in PM3 the most stable tautomer is II (it is more stable by 3.1 kcal than I and by 23 kcal than III). *Ab initio* calculations give somewhat different values, the most stable tautomer is I, which is 7.1 kcal more stable than II and 31.0 kcal than III. Table presents tautomeric composition of gossypol at 298 K calculated on the basis of energy stability analysis. The calculations confirm considerable effect of solvent nature on tautomeric equilibrium of gossypol. In polar solvent DMSO lactol form of gossypol dominates, whereas in nonpolar – aldehyde form and this fact is completely confirms with known experimental estimates. According to literary data, ketol form is present only in aqueous alkaline medium [3].

[1] Shmidt M.W., Baldridge K.K., Boatz J.A., *J. Comput. Chem.* **14** (1993) 1347–1363.
[2] B.Brzezinski, J.Olejnik, S.Paszyc, *Journal of Molecular Structure* **220** (1990) 261-268
[3] R.D. Stipanovic, A.A. Bell, C.R. Howell, *J. Am. Oil Chem. Soc.* (1973) 462.

DFT investigation of the tautomeric properties of substituted 1,5-benzodiazepinones-2

Sergiy I. Okovytyy[a,b], Ljudmila K. Svjatenko[c], Alexandr A. Gaponov[a], Liliya I. Kasyan[a], Igor N. Tarabara[a], and Jerzy Leszczynski[b]

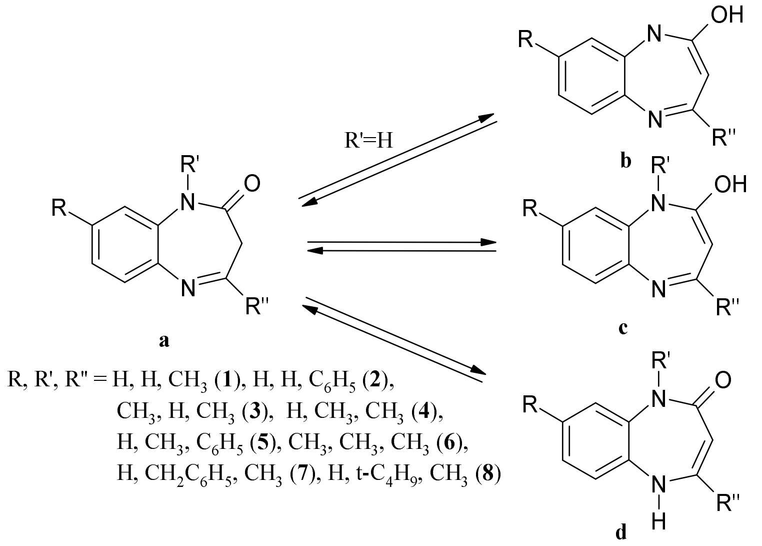
[a]*Dnepropetrovsk National University, Dnepropetrovsk, 49050, Ukraine,*

[b]*Computational Center for Molecular Structure and Interactions, Department of Chemistry, Jackson State University, Jackson, Mississippi 39217 USA*

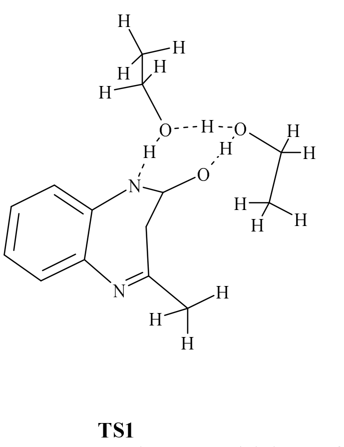
[c]*Kirovograd State Pedagogical University, Kirovograd, 25006, Ukraine*

The protomeris tautomerism of organic compounds is frequently considered to be an important property determining their reactivity. In the case of 1,5-benzodiazepinones-2 chemo-selectivity of alkylation, acylation, and other reactions strongly depends on the tautomeric equilibrium in the different solvents.

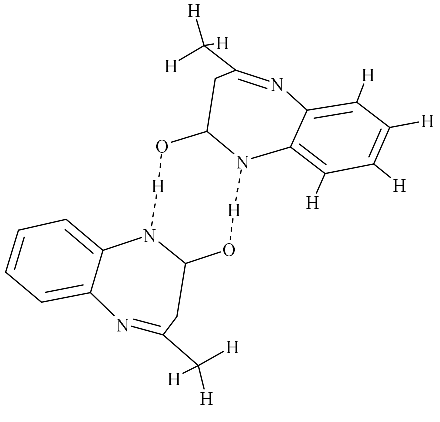
Here we present the results of quantum-chemical investigation of the thermodynamical stability of tautomers (**a – d**) for 1,5-benzodiazepinones-2 (**1 – 8**) and values of activation barriers for the corresponding proton-transfer processes performed at B3LYP/6-31G(d) level of theory.



R, R', R'' = H, H, CH_3 (**1**), H, H, C_6H_5 (**2**), CH_3, H, CH_3 (**3**), H, CH_3, CH_3 (**4**), H, CH_3, C_6H_5 (**5**), CH_3, CH_3, CH_3 (**6**), H, $CH_2C_6H_5$, CH_3 (**7**), H, t-C_4H_9, CH_3 (**8**)



TS1



TS2

According to calculations stability of tautomers decrease in the following row: a>d>b>c, while calculated for compound (**1**) values of activation barrier shows that kinetically the most probable tautomeric transformation is **1a**↔**1b**. In the case of ethanol solution two solvent molecules stabilize the transition state (**TS1**) and therefore substantially lower activation barrier. In aprotic solvents the most possible mechanism is self-mediated double proton transfer (**TS2**).

Investigation of reactions of superoxide anion (O_2^-) with alkyl bromides using nonempirical methods

A.F. Dmitruk, O.M. Zarechnaja, I.V. Efimova, A.I. Pomeshchenko, I.A. Opeida

L.M. Litvinenko Institute of physical-organic and coal chemistry NAS of Ukraine, Donetsk

The reactions of superoxide anion with alkyl halides are model for the study of chemical and biological activity of O_2^-. However, the mechanism of reactions of different substrates with O_2^- remains in discussion. In this work the results of nonempirical calculation of potential energy surfaces are presented for the different reactions of O_2^- with alkyl bromides:

$$RBr + O_2^- \rightarrow RO_2^{\bullet} + Br^- \quad (1)$$

$$RBr + O_2^- \rightarrow RH + HO_2^{\bullet} + Br^- \quad (2)$$

(where R = CH_3, C_2H_5, C_3H_7, C_4H_9).

Ab initio calculations were performed using GAMESS. Molecular structures were optimized in the base of MP2//DH with including of sp-diffuse and 1p-, 1f- and 1d-polarizations functions. Calculations of potential barriers for the reactions (1) and (2) ($\Delta E^{\neq}$) and imaginary frequencies ($v^{\neq}$) for possible transition states are presented in a table below.

R	$\Delta E^{\neq}$, kcal/mol		$v^{\neq}\cdot\mathbf{I}$, cm^{-1}	
	Reaction 1	Reaction 2	Reaction 1	Reaction 2
CH_3	2.1	-	538	-
C_2H_5	4.8	13.6	478	1639
C_3H_7	1.76	0.4	436	1550
C_4H_9	3.9	18.2	460	1765

The calculations results confirm increased substrate selectivity of O_2^- through the row of RBr homologues, which can result in substrate depending mechanism duality for the reactions of superoxide anion.

Calculated results qualitatively are in accordance with an experimentally obtained activation parameter for the reaction of $O_2^{\cdot -}$ with C_4H_9Br, value of activation energy for which is equal to a 15,1±0,5 kcal/mol.

Study of interaction of oxygen-containing monomers with maleic anhydride by methods of quantum chemistry

T.G. Tiurina, V.V. Zaitseva, A.V. Farafonova

National Academy of Sciences of Ukraine, L.M. Litvinenko Institute of physical-organic & coal chemistry, Donetsk, Ukraine

E-mail: zaitseva@infou.donetsk.ua

The donor-acceptor complexes of maleic anhydride (MA) with unsaturated compounds provide the receipt of alternating copolymers of MA, possessing set of valuable properties. The change of monomer reactivity in a complex is related to participating of definite molecule fragments in complex formation. Taking into account complication of experimental reveal of such centers for weak molecular complexes their structure were explored by semi-empirical quantum-chemical methods. Comparison of possibilities of parametrizing AM1 and PM3 (within the framework of the MOPAC 6 package) showed that procedure computation of geometry optimization with the algorithm EF by the method PM3 can not be fully completed for most considered molecules or molecular formations, while the method AM1 allows to carry out optimization with the norm of the RMS gradient 0.005-0.001.

We explored the interaction of maleic anhydride with styrene and oxygen-containing monomers - diallylftalate (DAF), diethylene glicole bis(allyl carbonate) (DEAK), a spiro-*ortho*-carbonate - 8-methyl-2-methylene-1,4,6,9-tetraoxaspiro[4,4]nonane (Sp-M), ketene acetal - 9-methyl-4-methylene-3,5-dioxabicyclo[5,4,0]undekane (KA), N-vinylpyrrolidone (VP). Formation of complexes between these compounds is confirmed by a ^{1}H NMR method. The found values of constants of complex formation (K, l/mol) diminish in series: VP (0.57) styrene (0.29) > KA (0.24) > DAF (0.23) > DEAK (0.19), that back tendencies of change of computation values of ionization potential of these donors ($I = E^{HOMO}$, eV): VP (8.96) < styrene (9.03) < KA (9.2) < DAF (10.2) < DEAK (10.4). The exception makes Sp-M for which K = 0.14 l/mol, and E^{HOMO}= 9.8 eV, that allows to suppose other character of interaction for the pair of Sp-M - MA on comparison with others. Within the framework of the method AM1 for every pair «donor - MA» a few configurations of complexes was revealed, corresponding to the local minima PPE. They are described by the values of $\Delta H = H^{compl} - \Sigma H^{mon}$, distances between the interactive groups of atoms, the change of charges on them. The sum of the acquired energetic, geometrical and electronic parameters allowed us to select three categories of complexes: formed due to interaction π-, H-bonds and the mixed type (with two centers of interaction), for which values of $-\Delta H$ are found within the limits of 0.5-1.2; 1.2-7.3 and 1.1-4.0 kcal/mol accordingly.

For Sp-M H-complexes configurations are found only, and for such donors, as styrene, DAF and KA the complexes of all types are formed. Practically for all configurations of complexes polarization of charges on the atoms of double bonds of molecules in them is discovered, activating these groups in the reaction of chain growth. The MA links with the break of cycle are found in the structure of copolymers backbone (NMR method), that experimentally confirms participation of H-complexes and complexes with two centers of interaction in the copolymerization process.

Thus, computation of structure of donor-acceptor complexes within the framework of the method AM1 allows to explain and to predict the passage of process of copolymerization for the systems of donor monomers with MA.

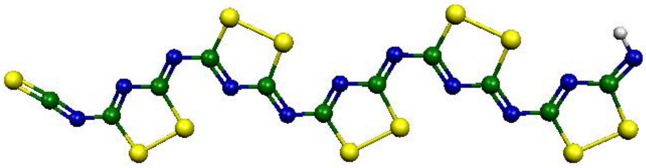
The structure of $(SCN)_x$. Clues from NMR parameters determined with Density Functional Theory

Herbert A. Früchtl[a], Tanja van Mourik[a], Chris J. Pickard[b] and J. Derek Woollins[a]

[a]***School of Chemistry, University of St Andrews, North Haugh, St. Andrews, Fife, KY16 9ST, Scotland, UK***

[b]***School of Physics & Astronomy, University of St Andrews, North Haugh, St. Andrews, Fife, KY16 9SS, Scotland, UK***

Although polythiocyanogen with the empirical formula $(SCN)_x$ was first reported in 1919 [1], the actual structure of this polymer is yet unknown. We have been attempting to determine the molecular structure of $(SCN)_x$ by considering a number of speculative structures proposed in the literature. By comparison of computed ^{13}C NMR chemical shifts with the observed data for the different proposed structures [2], we deduced that $(SCN)_x$ consists of linear chains based on 1,2,4-dithiazole units. A search over relaxed random periodic structures is consistent with this picture.



[1] E.E. Soderback, *Justus Liebigs Ann. Chem.* **419** (1919) 217.

[2] W.R. Bowman, C.J. Burchell, P. Likian, A.M.Z. Slawin, P. Wormald, J.D. Woollins, *Chem. Eur. J.* **12** (2006) 6366.

New representations about molecular structure N_2O_5 on the basis of quantum-chemical DFT calculations

I.I. Zaharov, A.I. Kolbasin, O.I. Zaharova, I.V. Kravchenko, V.I. Dyshlovoj

Volodymyr Dal East Ukrainian Natianal University, Severodonetsk Technological Institute, Severodonetsk 93400, Prosp. Radyanskyt, 59a, Ukraine

By quantum-chemical method of density functional theory DFT/B3LYP with use of the basis 6-311++G(3df) it is shown the energetics equivalence of molecular structures N_2O_5 with a C_S and a C_2 – symmetry (see fig. 1).

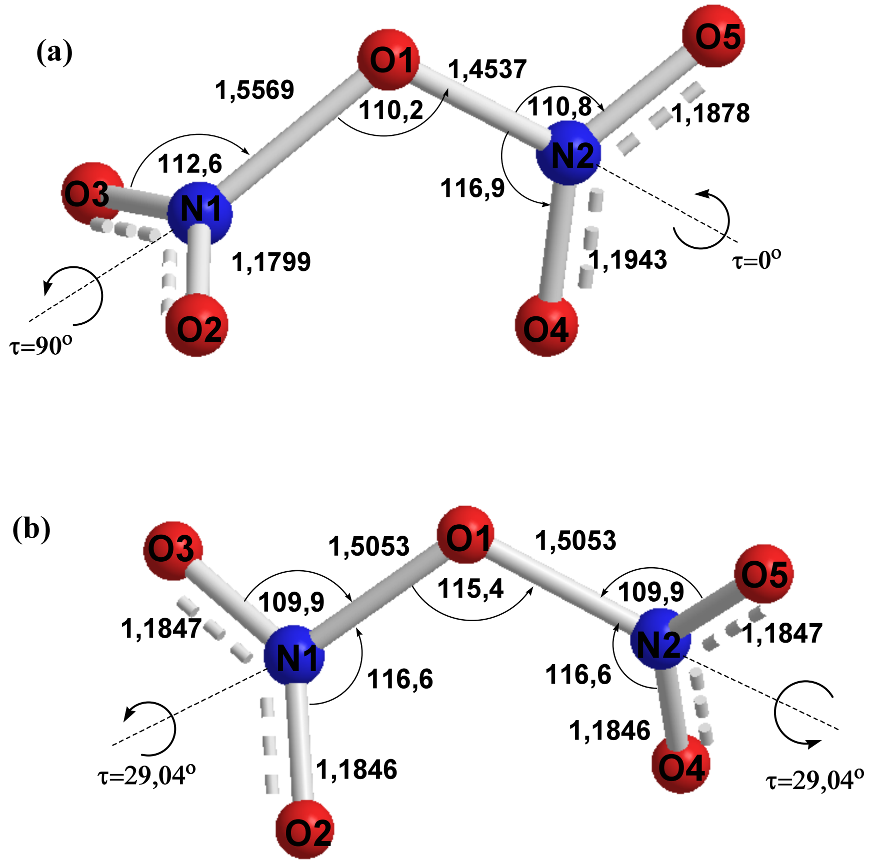


Fig. 1. Calculated by method B3LYP/6-311++G(3df) geometrical parameters (bond lengths in Å, angles in degrees) possible structures of molecule N_2O_5:
a) - C_S symmetry (τ_1=90°, τ_2=0°); **b)** - C_2 symmetry (the optimized values τ_1=29,04°, τ_2=29,04°). The dihedral angle τ corresponds to rotation of fragment NO_2 concerning a plane of a sheet.

The calculated vibration frequencies follow, that both equilibrium geometries characterize the real minima of potential energy and correspond to stationary states of the N_2O_5 molecule. On the basis of a comparison of the calculated and experimental vibrational spectra of N_2O_5 it is assumed, that the dinitrogen pentoxide in the gas represents the equiproportion mixture of the N_2O_5 molecules with the C_S and the C_2 symmetry, and in the solid phase the N_2O_5 is characterized by molecular structure of the C_S symmetry [1].

[1] I.I.Zaharov, A.I.Kolbasin, O.I.Zaharova, I.V.Kravchenko, V.I.Dyshlovoj, *Teoreticheskay i Eksperimental'naya Khimiya* **43**(1) (2007).

Prediction of reactivity of hexafluorocomplexes of p - d - elements of IVA and VA group

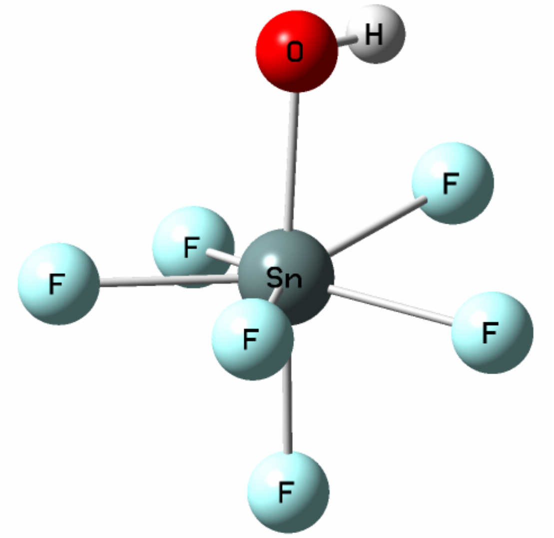
V. Plakhotnyk,[a] L. Yaryshkina[a], V. Rossikhin,[a] S.I. Okovytyy,[b,c] J. Leszczynski[c]

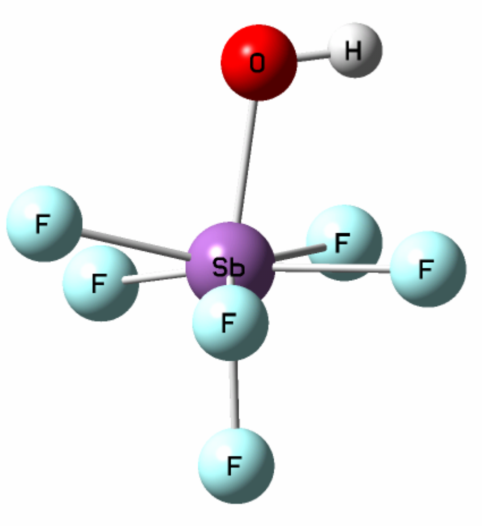
[a]Dnepropetrovsk National University of Railway Transport, Dnepropetrovsk, 49010, Ukraine e-mail: ecolab@email.dp.ua

[b]Dnepropetrovsk National University, Dnepropetrovsk, 49050, Ukraine

[c]Computational Center for Molecular Structure and Interactions, Jackson State University, Jackson, Mississippi, 39217, USA

In the row of $SiF_6^{2-} \rightarrow GeF_6^{2-} \rightarrow SnF_6^{2-}$ increasing of order number of an element results in extreme change of kinetic stability of hexafluorocomplex anion. Thus rate of alkaline hydrolysis from SiF_6^{2-} to GeF_6^{2-} essentially decreases, while from GeF_6^{2-} to SnF_6^{2-} increases. Investigation of kinetics and the mechanism of alkaline hydrolysis processes of these anions and performing of *ab initio* calculations of geometrical and electronic structure of different complexes has shown, that increasing of reactivity of SnF_6^{2-} in comparison with GeF_6^{2-} is caused by change of the mechanism of process, namely realization of the associative mechanism of the substitution, which includes formation of seven-coordinated Sn(IV) complex. We have carried out similar research for hexafluorocomplex of VA group for finding-out how general is the law of reactivity change of corresponding isoelectronic complexes containing 6 atoms of fluorine in internal coordination sphere. Experiment confirms, that hydrolysis of SiF_6^{2-}, GeF_6^{2-}, PF_6^{-} and AsF_6^{-} proceeds via dissociation mechanism, i.e. the transition state corresponds to elongation of one of X–F bonds. In that case increasing of the acceptor ability of XF_5 and X–F bond energy in XF_6^{n-} should result in the increasing of inertness of complexes which corresponds to experimental results. Moving from GeF_6^{2-} to SnF_6^{2-} the acceptor ability of SnF_5 significantly increases, so that another mechanism via seven-coordinated transition state with pentagonal bipyramide structure becomes possible (see structure bellow). As it has been shown, such changes result in increasing of the alkaline hydrolysis rate.





For elements of V group, such trend in changing of the mechanism if moving from AsF_6^{-} to SbF_6^{-} is even more probable. Our investigation of kinetics show that PF_6^{-} and AsF_6^{-} anions are very stable, while SbF_6^{2-} hydrolyzes very fast.

The quantum-chemical investigation of p-tolylsulfochloride aminolysis by cage amines

S.I. Okovytyy, A.V. Tokar, G.V. Gryn'ova, E.A. Isaev, L.I. Kasyan

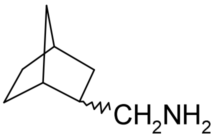
Dniepropetrovsk National University, 13 Nauchnaya st., Dniepropetrovsk, 49050, Ukraine

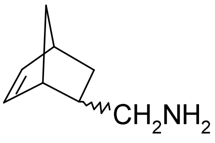
Aminolysis of sulfochlorides is one of the well-known synthetic methods, which allow to obtain sulfonamides:

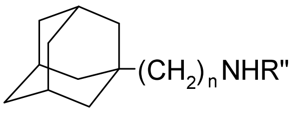
$$RSO_2Cl + NH_2R' \longrightarrow RSO_2NHR' + HCl, \quad \begin{array}{l} R=Alk, Ar, \\ R'=H, Alk \end{array}$$

The products of this reaction possess the wide spectrum of biological activity due to the presence of pharmacological fragments $–SO_2NH_2$ or $–SO_2NH–$ in their molecules. So, the sulfonamides are used as the components of many medicines. Consequently, the research of aminolysis process by methods of quantum chemistry has a great interest.

In this work we have been investigated the potential energy surface of p-tolylsulfochloride aminolysis by amines, which contain one of the following cage fragments - exo/endo-norbornyl, exo/endo-norbornenyl or 1-adamantyl:

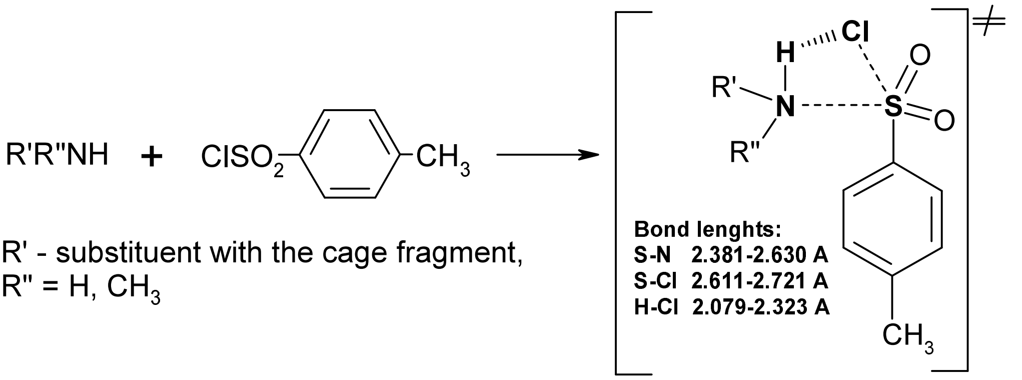






R''=H (n=0-2), CH_3 (n=0)

The calculations have been performed in gas phase and in solution (acetonitrile, ε=36,64) at PCM/B3LYP/6-31G(d)//B3LYP/6-31G(d) level of theory. The solvation effects have been evaluated by single-point calculations, i.e. with unrelaxed gas-phase isolated reactants (**I, II**) and transition states (**III**) geometries.



R' - substituent with the cage fragment,
R'' = H, CH_3

Bond lenghts:
S-N 2.381-2.630 A
S-Cl 2.611-2.721 A
H-Cl 2.079-2.323 A

I **II** **III**

The results of calculations have shown the preferable front side attack of amino-group on sulfur atom in comparison with corresponding back side approach. Some important regularities in correlation "structure – nucleophilic reactivity" for cage amines have been established. Thus, the entrance of withdrawing C=C-bond in norbornane fragment as well as exo/endo-isomerism of starting amines do not have any appreciable effects on calculated values of activation energy. On the contrary, the length of carbon chain $(CH_2)_n$ between the cage fragment and amino-group as well as the presence of substituent R" near nitrogen atom have a great importance for activation barriers of aminolysis reaction: these values have become much more high with decrease of n and introduction of $R''=CH_3$-group.

So, the obtained calculating data have demonstrated that the major factor of cage amines nucleophilic reactivity is the sterical factor.

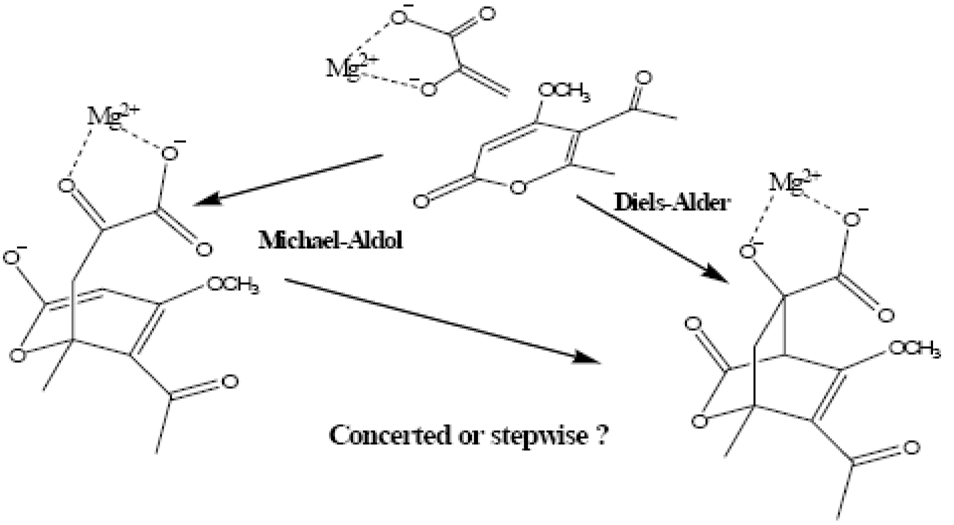
Theoretical study of a potential Diels-Alderase: The macrophomate synthase

Delphine Bas and Xavier Assfeld

Equipes de Chimie et Biochimie Théoriques, UMR 7565 - CNRS
Université Henri Poincaré, Nancy I, BP239, 54506 Vandoeuvre-lès-Nancy Cedex,France

The Diels-Alder reaction is one of the most fascinating organic reaction, both in terms of its synthetic potential and its reaction mechanism. Natural and synthetic enzymes potentially catalyzing this reaction, commonly named Diels-Alderases, have been widely studied due to their involvement in the biosynthesis of natural products.

The macrophomate synthase (MPS) from the phytopathogenic fungus Macrophoma commelinae that catalyzes the transformation of 2-pyrones derivatives to their benzoate analogs is believed to be one of them. The crystal structure [1] shows how the dienophile is held in place with the diene for the addition reaction. Nevertheless it does not distinguish between the concerted cycloaddition (Diels-Alder route) and the stepwise addition (Michael-aldol mechanism), two possible routes leading to the bicyclic intermediate.



The theoretical study presented here addresses the Diels-Alder versus Michael-aldol mechanism. Continuum and mixed quantum and molecular mechanics (QM/MM) calculations were performed to provide insights into both mechanisms aiming at a better understanding of the environment effects that can favour one or the other route.

[1] Ose et al., *Nature*, **422** (2003) 185-189.

Applications of Quantum Chemical Approaches to Some Environmental Problems

Yana Kholod,[a,b] Sergiy Okovytyy,[a,b] Leonid Gorb,[a] and Jerzy Leszczynski[a]

[a]Computational Center for Molecular Structure and Interactions, Jackson State University, Jackson, Mississippi, 39217, USA

[b]Dnepropetrovsk National University, Dnepropetrovsk, 49050, Ukraine

In the current work we demonstrate how quantum chemical methods can serve for resolving of some environmental problems at three stages:

a) prediction of physical and chemical properties of potential pollutants;
b) prediction of distribution of a substance of interest into environment;
c) design of degradation pathways and identification of products of decomposition of contaminants.

We employed computational techniques for investigation of conformational transitions and vibrational spectra of a nitramine CL-20. The mechanism of conformational transitions was studied. The method of determination of presence of each polymorphic phase in their mixture was proposed [1].

The physico-chemical properties, which determine distribution of a substance in the environment, such as vapor pressure, Henry's law constants, water solubility, octanol-water partition coefficients, heats of formation and ionization potentials, were studied using combination of DFT methods and COSMO-RS technique [2].

Several most important methods of decomposition of CL-20 (a toxic pollutant): unimolecular decomposition [3], alkaline hydrolysis [4, 5] and photodecomposition [6], were studied. We proposed possible mechanisms of decomposition and used ab initio calculations in combined experimental/theoretical studies for product identification.

[1] Y. Kholod, S. Okovytyy, G. Kuramshina, M. Qasim, L. Gorb, J. Leszczynski, *J. Mol. Struct.* (2007), In Press.
[2] M. Qasim, Y. Kholod, L. Gorb, D. Magers, P. Honea, J. Leszczynski, *Chemosphere* (2007), In Press.
[3] S. Okovytyy, Y. Kholod, M. Qasim, H. Fredrickson, J. Leszczynski, *J. Phys. Chem.* A **109** (2005) 2964-2970.
[4] M. Qasim, H. Fredrickson, P. Honea, J. Furey, J. Leszczynski, S. Okovytyy, J. Szecsody, Y. Kholod, *SAR and QSAR in Envir. Res.* **16** (2005) 495–515.
[5] Y. Kholod, S. Okovytyy, G. Kuramshina, M. Qasim, L. Gorb, J. Furey, P. Honea, H. Fredrickson, J. Leszczynski, *J. Mol. Struct.* **794** (2006) 288–302.
[6] Y. Kholod, S. Okovytyy, L. Gorb M. Qasim, J. Leszczynski. *Extended Abstracts of 15th Conference on Current trends in Computational Chemistry*, Jackson, MS, 2006, 96.

Prototropic tautomerism of uracil in model protein-nucleic acid contacts. Experimental and theoretical data

S.P. Samijlenko, Y.P. Yurenko, A.V. Stepanyugin, D.M. Hovorun

Institute of Molecular Biology and Genetics, National Academy of Sciences of Ukraine, vul. Zabolotnoho 150, Kyiv 03143, s.p.samijlenko@imbg.org.ua

The authors came across the problem of nucleotide bases' tautomerism when experimental investigation of elementary processes of protein- nucleic recognition *via* amino acid carboxylic group. In number of cases interpretation of ^{1}H NMR, UV and IR data was impossible without suggestion on tautomeric transformation of the bases in their complexes in anhydrous dimethylsulfoxide with deprotonated carboxylic group of the aspartic and glutamic acids' residues that was modeled by sodium acetate ($CH_3COO^-Na^+$).

Earlier quantum chemical calculations (at various theoretical levels) of energies of the adenine, isoguanine, purine and xanthine prototropic tautomer complexes with carboxylate ion in vacuum have evidenced tautomeric transitions from the ground-state to high-energy tautomeric forms, which agrees with experimental data.

As to uracil, essential transformation of its UV spectra upon interaction with sodium acetate and disappearance signals of both its imino protons in ^{1}H NMR spectra, accompanying by not large but trustworthy decrease in intensity of both bands of the carbonyl group stretching vibration ν(C=O). Results of quantum chemical calculations of the bases double complexes with carboxylate ion appeared incompatible with spectral data.

Only quantum chemical calculations of relative energies of triple complexes of Ura with carboxylate and sodium ions at the level of theory MP2/6-311++G(2df,pd)//B3LYP/6-311++G(d,p), taking into account BSSE and CPCM solvation model, made possible a consistent interpretation of spectroscopic data. The triple complex of the ground-state diketo-tautomer appeared the most stable, but complexes of enolic tautomers slightly exceed its in energy and under physiological temperature coexist with it. In all the triple complexes proton transfer occurs along H-bonds. As a consequence, the base imino protons are very labile: they transit from nitrogen atoms to oxygen atoms during enolic tautomers' formation, following by transfer to carboxylate ion. Since in the course of such transformations the base pass great number of intermediate energetic states, their signals cannot be registered in ^{1}H NMR spectra. Moderate, as compared to effects in ^{1}H NMR and UV spectra, decrease in the ν(C=O) bands' intensities is determined by those carbonyl groups of the bases, which become transformed to enolic ones. The two ν(C=O) bands of the ground-state triple complexes and a one band from each enolic complex are responsible for rather high intensity of carbonyl absorption in IR spectra.

Biological significance of the results obtained is discussed.

The Leading RNA Tertiary Interactions: Structures, Energies and Water Insertion of A-Minor and P-Interactions. A Quantum Chemical View

Judit E. Šponer,[a*] Kamila Réblová,[a] Ali Mokdad,[b] Vladimír Sychrovský,[a,c]
Jerzy Leszczynski[d], and Jiří Šponer[a,c*]

[a]Institute of Biophysics, Academy of Sciences of the Czech Republic, Královopolská 135, 612 65 Brno, Czech Republic

[b]Department of Biochemistry and Biophysics, School of Medicine, University of California at San Francisco, San Francisco, CA 94158

[c]Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, Flemingovo náměstí 2, 166 10 Prague 6, Czech Republic

[d]Department of Chemistry, Computational Center for Molecular Structure and Interactions, Jackson State University, Jackson, Mississippi 39217, USA

[*]Corresponding authors: judit@ncbr.chemi.muni.cz or sponer@ncbr.chemi.muni.cz

Complex molecular shapes of ribosomal RNA molecules are stabilized by recurrent types of tertiary interactions involving highly specific and conserved non-Watson-Crick base pairs, triples and quartets. We analyzed the intrinsic structure and stability of the P-motif and the four basic types of A-minor interactions (types I, II, III and 0) which represent the most prominent RNA tertiary interaction patterns refined in the course of evolution. In the studied interactions the electron correlation component of the stabilization usually exceeds the Hartree-Fock (HF) term, leading to a strikingly different balance of forces compared to standard base pairing stabilized primarily by the HF term. In other words, A-minor and P-interactions are considerably more influenced by the dispersion energy compared to canonical base pairs which makes them particularly suitable to zip the folded RNA structures which are substantially hydrated even in their interior. Among the studied systems the strong A-minor II and weak A-minor III interactions require water molecules to stabilize the experimental geometry. Gas phase optimization of the canonical A-minor II A/CG triple without water results in geometry which is clearly inconsistent with the RNA structure. The gas phase structure of the P-interaction and the most stable A-minor I interaction nicely agrees with the geometries occurring in ribosome. A-minor I can also adopt an alternative water mediated substate rather often observed in x-ray and molecular dynamics studies. The A-minor I water bridge, however, does not appear to stabilize the tertiary contact and its role is to provide structural flexibility. The insertion of polar water molecule in the A-minor I A/CG tertiary contact occurs into the A/C tertiary pair stabilized primarily by the HF (electrostatic) interaction energy while the dispersion-controlled A/G contact remains firmly bound. Thus, the intrinsic balance of forces as revealed by the QM calculations nicely correlates with many aspects of the behavior of the studied interactions inside RNA. We also briefly discuss the non-negligible methodological differences when evaluating simple base – base nucleic acids base pairs and the complex RNA tertiary base pairing patterns using QM procedures.

(a) Šponer, J.E.; Špačková, N.; Kulhánek, P.; Leszczynski, J.; Šponer, J. *J. Phys. Chem. A* **109** (2005) 2292-2301. (b) Šponer, J.E.; Špačková, N.; Leszczynski, J.; Šponer, J. *J. Phys. Chem. B* **109** (2005) 11399-11410. (c) Šponer, J.E.; Leszczynski, J.; Sychrovsky V.; Šponer, J. *J. Phys. Chem. B* **109** (2005) 18680-18689. (d) Mokdad, A.; Krasovska, M.V.; Šponer, J.; Leontis, N.B. *Nucleic Acids Res.* **34** (2006) 1326-1341.

Ab initio Post-Hartree-Fock Study of M-DNA Fragments: molecular and Electronic Structure of AT and GC pairs with Zn $^{2+}$

Yu. V. Rubin[a], L.F. Belous[a], A.A. Yakuba[b]

[a]B.I. Verkin Institute for Low Temperature Physics and Engineering, NANU, Kharkov
[b]V.M.Glushkov Institute of Cybernetics, NANU, Kiev

To study physical properties of fragments of metallic DNA (M-DNA), molecular and electronic structures and thermodynamic characteristics of adenine-thymine and guanine-cytosine pairs with Zn^{2+} ion (the ion was placed between nucleic acid bases) and of components forming these pairs were calculated at MP2/6-31+G* level of theory. As well, calculations were performed for adenine-thymine-Zn^{2+}-hydroxyl and guanine-cytosine-Zn^{2+} -hydroxyl complexes. It was revealed that bond lengths changed in three- and four-member complexes: on the fragment close by the site of interaction with Zn^{2+} (N3-C2-N1-C6-N10 fragment) in adenine, on C2-N3-C4-C5-C6-N1 fragment on the pyrimidine ring and on C6-O10 in guanine, in comparison with neutral molecules. Charges on atoms changed at the same fragments. In the complexes calculated the interaction energies of base pairs of with Zn^{2+} are significantly higher than that of iminoproton with AT and GC pairs or that of Zn^{2+} with its hydrate shell (6 water molecules). HOMO and LUMO analysis of the ATZn+ triple complex and AT pair showed the increase of sizes of triple complex LUMO, which points to a possibility of electron delocalization over the whole complex. A mechanism of electric current in M-DNA is discussed.

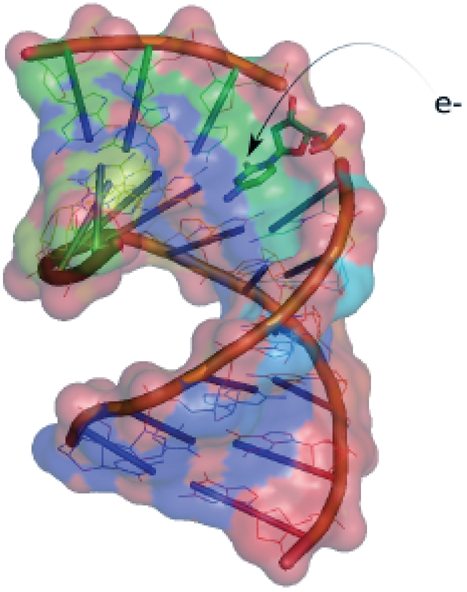
QM/MM Investigation of Single-Strand Breaks Induced by Low-Energy Electrons in DNA

Pierre-François Loos[1] and Xavier Assfeld[2]

Equipes de Chimie et Biochimie Théoriques, UMR 7565 - CNRS UHP

Institut Jean Barriol (FR CNRS 2843), Faculté des Sciences et Techniques, Nancy-Université, B.P. 239, 54506 Vandoeuvre-lès-Nancy Cedex, France

Recent experiments have shown that low-energy electrons (0.1-2 eV) can induce single-strand breaks (SSBs) in DNA [1]. Understanding these mechanisms is of great importance for the developement of medicinal sciences. Previous studies on model systems demonstrate that low-energy electrons induce the covalent-bond cleavage in DNA according to a through-bond electron transfer process between the π^* orbitals of the nucleic base and a specific bond [2, 3]. It has been shown that the $C_{3'}$-$O_{3'}$ σ sugar bond rupture dominates the SSBs of DNA [3]. Within the LSCF/MM method [4], we examine the effect of including the neighboring nucleotides at the molecular mechanic (MM) level using the Amber *ff99* force field. Because of the spatially-extended behaviour of this phenomenon, the whole nucleotide where the bond cleavage occurred must be included in the quantum mechanical (QM) part that is treat at the B3LYP/6-311+G* level of theory.



[1] Boudaiffa, B.; Cloutier, P.; Hunting, D.; Huels, M. A.; Shance, L. *Science* **287** (2000) 1658.
[2] Simons, J. *Acc. Chem. Res.* **39** (2006) 772.
[3] Gu, J.; Wang, J.; Leszczynski, J. *J. Am. Chem. Soc.* **128** (2006) 9322.
[4] Assfeld, X.; Rivail, J.-L., *Chem. Phys. Lett.* **263** (1996) 100.

---

[1] Electronic address: Pierre-Francois.Loos@cbt.uhp-nancy.fr
[2] Electronic address: Xavier.Assfeld@cbt.uhp-nancy.fr

An *ab initio* quantum chemical study of the nature of spontaneous point errors in DNA biosynthesis

O.S. Kochina[a] and D.M. Hovorun[b]

[a] ***Taras Shevchenko Kyiv National University, Faculty of Radiophysics, pr. Hlushkova 2, korp 5, Kyiv, 03127, Ukraine, kochina_olga@inbox.ru***

[b] ***Institute of Molecular Biology and Genetics, National Academy of Sciences of Ukraine, vul. Zabolotnoho 150, Kyiv, 03143, Ukraine***

The nature of spontaneous point errors in DNA enzymatic synthesis is among the most urgent problems of molecular biology and quantum biophysics. This important topic has been discussed over fifty years and now needs of new ideas and approaches [1].

We suggest here a new approach to the old problem based on *ab initio* quantum chemical calculations at the MP2/6-311++G(d,p)//DFT B3LYP/6-31G(d,p) theory level.

Our approach proceeds from the assumption that in active sites of high fidelity DNA polymerases a template nucleotide is rigidly fixed in space whereas an incoming nucleotide adjusts to it. The chemical stage of the reaction takes place when mutual arrangement of both nucleotides is close to one in Watson-Crick pair.

To verify this idea, geometry and energetics of 25 purine-purine and purine-pyrimidine base pairs, capable of incorporating into double helical DNA, were studied. At that all possible bases' tautomeric forms as well as orientations against the sugar-phosphate backbone (syn and anti) were taken into account.

The obtained results confirm and quantitatively substantiate Watson-Crick [2], Topal and Fresco [3] hypotheses, postulating bases' prototropic tautomerism to be the main source of spontaneous point mutations in the course of DNA biosynthesis. As regards successful replication of a point mutation, the main structural advantage of rare tautomeric pairs consists in their quasi-isomorphism with Watson-Crick pairs. In the cases of mispairing with bases in canonical tautomeric forms, steric hindrances prevent the quasi-isomorphic state formation. It can be inferred from the calculations that the following purine-purine and purine-pyrimidine pairs -A-C*, T-G*, A*-G*syn and G*syn-G*syn- (star indicates a rare tautomer, syn denotes a syn orientation of the base) are the most likely candidates for explanation of spontaneous point mutations in DNA.

[1] V.I. Danilov, V.M. Anisimov, N. Kurita, D.M. Hovorun, *Chem. Phys. Lett.* **412** (2005) 285-293.
[2] J.D. Watson, F.H.C. Crick, *Cold Spring Harbor Symposia on Quant. Biol.* **18** (1953) 123-131.
[3] M.D. Topal, J.R. Fresco, *Nature* **263** (1976) 285-289.

Deformability of Structure and Intramolecular Hydrogen Bonds in Canonical 2'-Deoxyribonucleotides From Viewpoint of Incorporation to Diferent Types of DNA

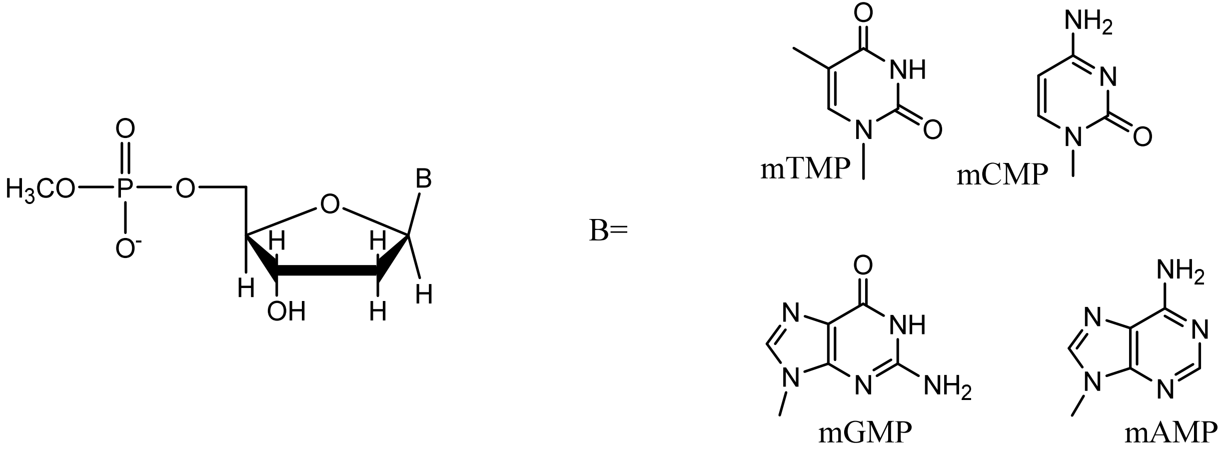
Gennady V. Palamarchuk[a,b], Oleg V. Shishkin[a,b,c], Leonid Gorb[b,c],
Jerzy Leszczynski[b,c]

[a]STC "Institute for Single Crystals," National Academy of Science of Ukraine, 60 Lenina Ave., Kharkiv 61001, Ukraine

[b]Ukrainian-American Laboratory of Computational Chemistry, Kharkiv, Ukraine, and Jackson, Mississippi, USA

[c]Computational Center for Molecular Structure and Interactions, Jackson State University, 39217 Jackson, MS, USA

The main interest to canonical 2'-deoxyribonucleotides(DNT) is caused by fact that they are building blocks of DNA. Incorporation of DNTs require some changes of their conformation. Character and energetic of such deformations provide information about possible inherent strain of DNA macromolecules.



The molecular structure of methyl ethers of 2'-deoxyribonucleotides was calculated using the density functional theory with B3LYP/aug-cc-pvdz method. An analysis of the electron density distribution was carried out within Bader's "Atoms in Molecules" (AIM) approach using the B3LYP/aug-cc-pvdz wave function.

Results of calculations demonstrate that the formation of A-form of DNA demands smaller amount of energy for the deformation of the geometry of nucleotides. The smallest deformations are observed for mGMP. The largest increase of energy is found for C-form of DNA. However, in this case the smallest deformation energy is observed for mCMP and the highest for mGMP. It is interesting to note, that the energy of deformation of pairs of nucleotides A+T and G+C in each form of DNA is almost identical. They are 4.8 kcal/mol for A-DNA, 13.1-13.2 kcal/mol for B-DNA and 16.8 kcal/mol for C-DNA. Thus, formation of Watson-Crick AT and GC pairs of nucleotides is almost equivalent from viewpoint of energy required for deformation of nucleotides geometry.

Analysis of the electron density distribution reveals that every type of DNA has the unique set of intramolecular hydrogen bonds. So, for A-form of DNA the C6(8)-H...O5' bond is reference (in case C6-H...O5' for pyrimidine and C8-H...O5' for purine nucleotides). For B,C and D-forms of DNA C6(8)-H...O-P bond is reference. And in B-and D-forms of DNA intramolecular hydrogen C2'-H...O5' bond is observing. Deformation of nucleoptides due to incorporation to DNA macromolecules results in weakening of intramolecular hydrogen bonds except A-DNA.

Computer simulation of interaction of actinocin derivative with DNA fragments of different sequence

A. M. Golius[a], K. V. Miroshnychenko[b], A. V. Shestopalova[b]

[a]*Karazin Kharkiv National University, 4 Svoboda Sq., Kharkiv, 61077, Ukraine*

[b]*Usikov Institute of Radiophysics and Electronics of National Academy of Sciences of Ukraine, 12 Ak. Proskura Str., Kharkiv, 61085, Ukraine*

The objective of this study was to investigate the interaction of DNA fragments of different sequence and a derivative of anticancer antibiotic actinomycin D with asymmetric side chains (actIII-II) by means of computer simulation using molecular docking method. The structure of actIII-II is shown in Figure 1. The conformation of actIII-II was optimized in the program Gaussian03 using b3lyp method with the 6-31G* basis set. For the obtained structure, the electrostatic potential was calculated in the program GAMESS by Hartree-Fock method with the 6-31G* basis set, which was used then for the derivation of the actIII-II atomic charges according to the RESP-methodology. The received charges can be used in the molecular dynamics simulation with the AMBER force field.

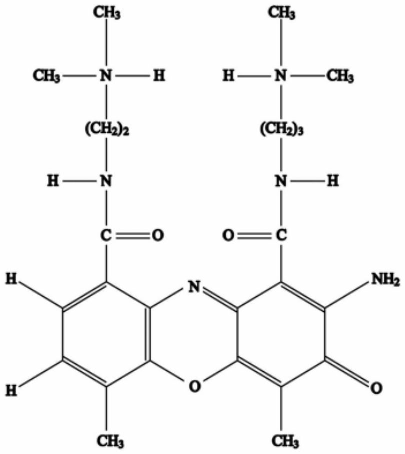


Figure 1. The structure of actinocin derivative actIII-II

In order to estimate the sequence specifity of binding of actIII-II, eight DNA dodecamers differing by the central tetramer sequence were taken. The DNA sequences that are known to bind with actinomycin D were considered. For each of the dodecamers, 10 ns molecular dynamics trajectory was calculated in the program package AMBER 9 using parm98 parameter set with the explicit representation of water and counterions. As a result of the trajectory cluster analysis, 7-9 conformations were chosen for every DNA sequence. They were used as targets for the molecular docking simulation with actIII-II. The molecular docking was performed in the program package AutoDock 3.05 using Lamarckian genetic algorithm. The most probable complexes were selected relying on the following criteria: the minimum energy of complex, the maximum number of hydrogen bonds in the complex between actIII-II and DNA, and the good reproducibility of complex. For all DNA sequences, three main types of complexes were obtained: the binding of actIII-II in the DNA minor groove with the long axis of the chromophore being perpendicular to the minor groove (I); the binding of actIII-II in the DNA minor groove with the long axis of the chromophore lying along the minor groove (II); and the binding of actIII-II in the DNA major groove (III). The complex of type (I) was found to be the most energetically favorable for the majority of DNA sequences. The difference of binding energies of actIII-II with different DNA sequences was about 2 kcal/mol. Some preference of binding was observed for the TGCT sequence.

Molecular dynamics simulation of DNA dodecamers of different sequence

K. V. Miroshnychenko, A. V. Shestopalova

Usikov Institute of Radiophysics and Electronics of National Academy of Sciences of Ukraine, 12 Ak. Proskura Str., Kharkiv, 61085, Ukraine

Many anticancer antibiotics exert their biological activity due to the interaction with DNA molecules as intercalators or minor groove binders. The objective of this research work was to investigate by means of molecular dynamics simulation the structure and dynamics of DNA dodecamers of different sequence and to create the local database of DNA dodecamers molecular dynamics trajectories in order to use them as targets for anticancer antibiotic derivatives.

Eight DNA dodecamers differing by the central tetramer sequence were chosen as the objects for the investigation: $d(CGCGXXXXCGCG)_2$, were XXXX = AATT, AGCG, AGCT, ATAT, GTCA, TGCA, TGCT, TTAA. Dodecamers sequences with available X-ray structure at a good resolution and those that are known to bind anticancer antibiotic actinomycin D were considered. The starting structures were taken from the Nucleic Acid Database or were built in the Arnott B-DNA canonical form using NUCGEN module of the AMBER 9 package in the case when there was no X-ray structure. The molecular dynamics simulations were carried out in the program package AMBER 9 with the parm98 and parm99 parameter sets and explicit representation of water and counterions. For all of the investigated dodecamers, stable 10 ns molecular dynamics trajectories were obtained. The root-mean-square deviation, calculated with respect to the first trajectory frame, was found to be 2.6-2.8 Å. The hydrogen bonds between bases in base pairs, except terminal residues, well conserved during all the trajectory. The conformational analysis of sugars revealed that the majority of them were in the C2'-endo form.

In order to determine the influence of DNA sequence on the collective motions of dodecamers atoms, the analysis of trajectories by essential dynamics method was carried out. It showed that independently of sequence, the first 45 eigenvectors of the covariance matrix built from the molecular dynamics trajectory would be enough for the description of 90% of all atomic positional fluctuations observed in the dodecamer simulation. The force constants, associated with the eigenvectors, were found to be the lowest for the $d(CGCGTTAACGCG)_2$ dodecamer indicating that this sequence was the most easily deformable. The absolute similarity indices, calculated for the motions of atoms of sugar-phosphate backbones of different dodecamers using the first 500 eigenvectors, were found to be in the range of 0.7-0.9. The configurational entropy estimates revealed no evident influence of sequence on the conformational mobility of the dodecamer with the TTAA sequence being slightly more flexible than the other ones.

Structural dynamics of ribozymes studied by MD simulations

Maryna V. Krasovska[a,b,] Jana Sefcikova[c], Maria M. Rhodes[c], Naďa Špačková[a], Kamila Réblová[a], Nils G. Walter[c] and Jiří Šponer[a]

[a]*Institute of Biophysics, Academy of Sciences of the Czech Republic, Královopolská 135, 612 65 Brno, Czech Republic*

[b]*Institute for Single Crystals, Academy of Science of Ukraine, Kharkov, Ukraine*

[c]*Department of Chemistry, Single Molecule Analysis Group, University of Michigan, 930 N. University Avenue, Ann Arbor, MI 48109-1055, USA*

The Hepatitis Delta Virus (HDV) ribozyme is an RNA enzyme crucial for replication of HDV, which causes leaver disease in humans. We have analyzed a total of ~400 ns of explicit-solvent molecular dynamics (MD) simulations to provide a complementary atomistic view of the active site dynamics and binding of monovalent and divalent cations as well as water molecules to reaction precursor and product forms of the HDV ribozyme. Along with x-ray crystal structures our results are consistent with a concerted reaction mechanism in which C75 and hydrated Mg^{2+} act as general base and acid, respectively. Simulations reveal a role of loop L3 as a flexible structural element to facilitate conformational switch induced by cleavage reaction. L3 also controls the electrostatic environment of the catalytic core, which in turn likely modulates C75 base strength and metal ion binding. Monovalent cations bind to the active site and elsewhere assisted by structurally bridging long-residency water molecules, but are generally delocalized. Simulations of HDVr are contrasted with structural dynamics of Hairpin ribozyme (HrRz). HrRz, similarly to HDVr, creates a unique pocket of deep negative electrostatic potential (ESP) in its catalytic center. In contrast to HDVr, however, the closed HrRz ESP pocket is not suitable to interact with ions and is filled by a chain of highly structured waters instead. We suggest that these water molecules are directly involved in catalysis.

[1] M.V. Krasovska, J. Sefcikova, N. Spackova, J. Sponer and N.G. Walter: Structural dynamics of precursor and product of the RNA enzyme from the Hepatitis Delta Virus as revealed by molecular dynamics simulations. *J. Mol. Biol.* **351** (2005) 731-748.

[2] M.V. Krasovska, J. Sefcikova, K. Reblova, B. Schneider, N. G. Walter and J. Sponer: Cations and hydration in catalytic RNA: Molecular dynamics of the hepatitis delta virus ribozyme. *Biophys. J.* **91** (2006) 626-638.

[3] M.M. Rhodes, K. Reblova, J. Sponer and N.G. Walter: Trapped water molecules are essential to structural dynamics and function of a ribozyme. *Proc. Natl. Acad. Sci. USA* **103** (2006) 13380-13385.

[4] J. Sefcikova, M.V. Krasovska, J. Sponer and N. G. Walter: The genomic HDV ribozyme utilizes a previously unnoticed U-turn motif to accomplish fast site-specific catalysis. *Nucl. Acids Res.* **35** (2007) 1933-1946.

[5] J. Sefcikova, M.V.Krasovska, N. Spackova, J. Sponer and N.G. Walter: Impact of an extruded nucleotide on cleavage activity and dynamic catalytic core conformation of the Hepatitis Delta Virus ribozyme. *Biopolymers* **85** (2007) 392-406.

AFM study and computer modeling of DNA-wrapped carbon nanotube

M.V. Karachevtsev[a], O.S. Lytvyn[b], V.S. Leontiev[a], S.G. Stepanian[a],
and V.A. Karachevtsev[a]

[a]B.I.Verkin Institute for Low Temperature Physics and Engineering, Kharkov, 61103, Ukraine

[b]V. Lashkaryov Institute of Semiconductor Physics, Kyiv, 03028, Ukraine

Bionanohybrids of carbon single-walled nanotubes (SWNT) with fragmented single (ss DNA) or polyC were studied by Atom Force Microscopy (AFM) and computer modeling. It was found that the fragments of the polymer wrap in several layers around the nanotube forming a strand-like spindle. The AFM height analysis of the hybrid showed the stepped increase of the polymer thickness above the nanotube surface. The height of the step above the first layer is varied from 0.5 till 0.8 nm.

The hybrids of SWNT with single-, double- or triple strands of the biopolymers were simulated using the Amber force field. It was shown that such structures are stable. Analysis of the structures of the SWNT:polyC hybrids permits to reveal the presence of different contacts between the polymer and nanotube as well as between polyC strands wrapped around the nanotube in multi layers. From this analysis we found three possible interchain cytosine-cytosine contacts which may be modeled by the following cytosine dimers: dimer with two N_{amino}-H···N_{cycle} H-bonds, dimer with N_{amino}-H···N_{cycle} and N_{amino}-H···N_{amino} H bonds and dimer with N_{amino}-H···O=C H-bond. Molecular contact due to the H-bonds between cytosine amino groups and phosphate group oxygens was also observed. Structures of the cytosine-cytosine dimers as well as dimers consisted of cytosine and the component of polyC were calculated at the B3LYP/6-31++G** level of theory. We also calculated the BSSE corrected interaction energy in the stacking complex of cytosine with the zigzag (10, 0) SWNTs at the MP-2 level of theory.

Quantum chemical analysis of motive forces of interactions between silica nanoparticles and erythrocytes

O.M. Tsendra, V.V. Lobanov

O.O. Chuiko Institute of Surface Chemistry, National Academy of Sciences of Ukraine, General Naumov str. 17, Kyiv 03164, Ukraine

Information about the interaction mechanism between oxide nanoparticles (usually SiO_2) and cells (in particular red blood cells) are very important for use of biocomposites in medicine and biology. It is well known that surfaces of silica nanoparticles and erythrocytes are negatively charged. In order to explain experimentally observed agglutination, it is necessary to consider positively charged ions as bonding intermediates, particularly hydrated protons formed due to the electrolytic dissociation of acidic surface groups of SiO_2 nanoparticles and some molecules on the external surface of cell membranes.

This study considers results from quantum-chemical calculations on the interaction between SiO2-nanoparticles and a cell membrane lipid area. To represent a cell membrane a cluster consisting of a complex of phosphatidylcholine (PHCH) and cholesterol (CHL) molecules was chosen. For simplification of calculations, the number of carbon atoms in fatty radicals was shortened up to 4. The complex formed by PHCH and CHL molecules was considered as negatively charged due to dissociation of the cholesterol molecule. The silica fragment was simulated with the globule-like cluster $Si_{10}O_{28}H_{16}$ of adamantine (β-cluster). One proton of silanol group in β-cluster was believed to be removed, so that the total charge was equal to -1.

A supramolecular zero-charged structure consisting of a β-cluster (charge of negative -1), two compound cations $[H_2O\cdots H\cdots OH_2]^+$, and a complex $(PHCH{\cdot}CHL)^-$ was considered. It was shown that when the distance between system components is large enough, the interactions is controlled by electrostatic forces. When the distances between objects reached some critical value, the anions of SiO_2 and the lipid complex saturated the localized negatively-charged sites with protons from the $[H_2O\cdots H\cdots OH_2]^+$ cations. The resulting neutral components of the dispersed system interact, water molecules being involved which are intermediates of a hydrogen bond network.

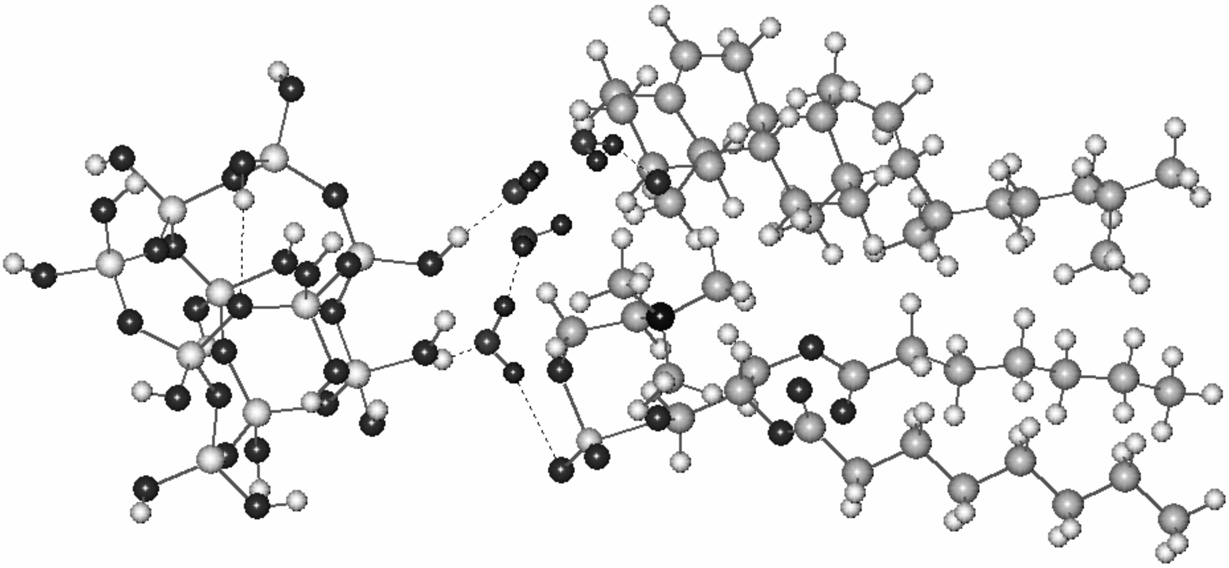


Fig. Equilibrium spatial structure of a complex where water molecules provide binding between a fragment of SiO_2 surface and cell membrane lipid area.

The calculations were carried out by means of quantum chemical SCF MO LCAO methods within the framework of PM3 valence-only approximation. All the geometric parameters of the supramolecular structures were optimized.

Quantum chemical modelling, IR- and mass-spectrometry of ionic clusters based on biomedical calcium phosphates

I. Boldeskul [a], L. Sukhodub [a], V. Khavryuchenko [c]

[a]Institute of Applied Physics, National Academy of Sciences of Ukraine, 040034 Sumy, 58 Petropavlovskaya st.

[b]Institute of Sorption and Ecology Problems, National Academy of Sciences of Ukraine.03164 Kiev, 13 Generala Naumova st.; e-mail: vkhavr@compchem.kiev.ua

Obtaining, control and analysis of biomedical materials based on hydroxyapatites is impossible without using modern instrumental devices [1]. Complex phase composition and mutual transformation of components require simultaneous application of different physical techniques for correct structure formation in synthetic process and adequate description of the product.

The lecture deals with some peculiarities of calcium phosphate vibration spectra that might have practical significance, as well as potential usage of vibration spectroscopy as a reference method for the laboratory and industrial diagnostics, expertise including.

Characteristicity of vibrations and peculiarities of spectral and structure behaviour of phosphate- and carbonate-ions, calcium oxide and hydroxyl functional groups, as well as their sensitivity to intra- and intermolecular interactions, crystal effects including, allow us to suggest effective application of IR- and Raman spectroscopy for cluster formation analysis. The informative potential of vibration spectroscopy grows significantly due to the inelastic neutron scattering (INS) spectra as well as mass-spectrometry of matter in various phasal states.

Specific attention is drawn to quantum-chemical calculation and computer modelling that provide additional possibilities to study structures which model elementary segment of the amorphous phase within the frames of ***ab initio*** method using MINI basis set. Experimental data are compared with the results of cluster modelling of hydroxyapatites, tricalcium phosphate, calcium oxide and ions, including complete normal-coordinate analysis of corresponding vibrational spectra. By increasing cluster size we will be able to describe the system more adequately and accurately.

[1] A.P.Shpak, V.L.Karbovski,V.V.Trachevski, APATITES, Kiev, Academperiodika, 2002.

Conformation of 106-177 fragment and disposition of Ia subdomain of human serum albumin

I.E. Shchechkin, T.O. Hushcha

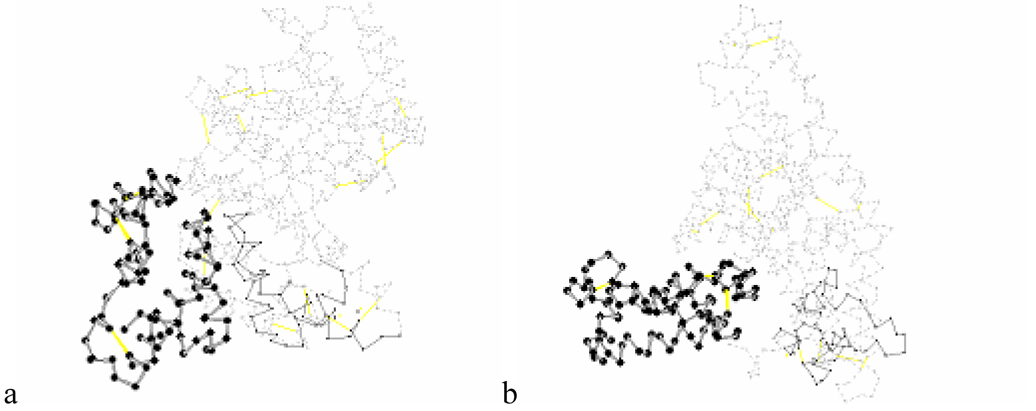
Institute of Bioorganic Chemistry and Petrochemistry, National Academy of Science of Ukraine, 1 Murmanska str., 02660, Kyiv-94, Ukraine, e-mail: shch406@bpci.kiev.ua

Loops and loop-like motifs of proteins are famous for their important role in protein function, like tuning a protein-ligand fitting and gating their interactions. One may suggest that loops serve as check-pieces unleashing relative domain-domain movement by means of rotation around its ends, coming out of a globule to outer solvent and distorting the interactions, which define relative domain-domain spatial disposition.

To examine the possibility of such change we investigated the 119-170 loop-like motif of human serum albumin (HSA). The feature of this fragment spatial disposition in the native state consists in its ends located on the globule surface, and the middle part embedded deeply into the globule interior between the Ia subdomain and the rest of the molecule. We designed a solvent exposed unstrained conformation of the 119-170 loop-like motif and studied, how the conformational transition affects the Ia subdomain disposition with respect to the protein globule.

First we constructed some initial conformation of the loop-like motif that was elongated and directed outside the globule while its secondary structure helices were conserved. The obtained structure was very strained. So, lest the structure of the globule should be considerably unfolded during energy minimization, the internal energy of the 119-170 chain fragment was relaxed on the condition of keeping a fixed distance between the fragment ending groups. Further we handled an extended model, where the fragment 106-172, comprising the turns 106-118 and 171-172 together with the loop-like motif 119-170, was treated as a flexible bridge between the Ia subdomain and the rest of the molecule. To overcome local minima problem minimizing energy we utilized our *component alternation* scheme taking bond constraining potential, helix structure forcing potential and real pairwise intra protein potential energy as the components to alternate. The final stage consisted in minimization of the whole energy, including solvation terms.

The resulting conformation is unstrained and not appreciably unfolded, helix structure within flexible fragment is destroyed with helix-forming hydrogen bonds in it substituted with solvation interactions, loop-like motif 119-170 is located entirely at the surface of the molecule, and the subdomain Ia changed its disposition in the globule. For comparison, the native conformation treated in the same model has been undergone the energy minimization procedure, what showed this conformation is about optimal. Its energy is close to that of the new obtained conformation; furthermore, the latter appeared even something more stable. In the new conformation steric strain is greater but solvent polarization energy is lower as compared to native optimized one.



Subdomain Ia (bold) and 119-170 loop-like motif (fine solid) in native optimized (a) and new obtained (b) conformations.

Effect of alkaline solution on the reactivity of epoxyendic imide. A DFT study

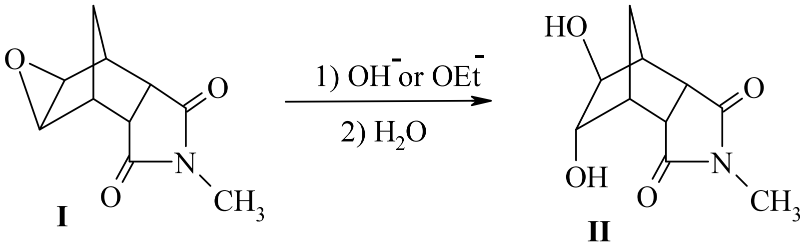
T. Petrova,[a,b] S. Okovytyy,[a,b] I. Tarabara,[b] L. Gorb,[a] J. Leszczynski[a]

[a]*Department of Chemistry, Computational Center for Molecular Structure and Interactions, Jackson State University, 1400 J.R. Lynch Street, P.O. Box 17910, Jackson, MS 39217-0510, USA*

[b]*Department of Organic Chemistry, Dnepropetrovsk National University, Dnepropetrovsk 49625, Ukraine*

An interest to the reactivity of nitrogencontainig bicyclic compounds has been induced due to substantial pharmacophoric properties of bicyclic skeleton. Rigid structures of norbornene derivatives with fixed orientation of substituents represent convenient models for investigation of the structure-biological activity relationships. For this purposes, the development of new synthetic techniques for the transformation of norbornene epoxyimides into geterocyclic compounds in alkaline media was performed. A theoretical investigation of possible synthetic pathways in such systems also is very important in this field.

The nucleophilic substitution reaction of epoxyimide (**I**) with either hydroxy- or ethoxy-anion is expected to result in formation of amidolactone, while it results experimentally in isolation of the single product - trans-dihydroxiimide (**II**).



In the present work a quantum-chemical investigation of potential energy surfaces for the alkaline hydrolysis and ethanolysis reactions of epoxyendic imide (**I**) has been carried out. The calculations have been performed at the B3LYP/6-31+G(d) level of theory in the gas phase and in the solution(polarizable continuum model). All critical points were further characterized by analytic computations of harmonic vibrational frequencies at the same levels of theory.

Experimentally a nucleophlic substitution of imides is believed to include two major reaction steps. The first step is formation of an anionic tetrahedral intermediate. The second step is decomposition of the intermediate to the products. Epoxyimides can interact with nucleophilic agents, namely with carbon atoms of carboxyimide part.

Different possible pathways of the alkaline hydrolysis and ethanolysis reaction were investigated and compared. According to the results the reaction starts from the addition of anion to carbonyl carbon atom of the imide cycle with formation of the tetrahedral intermediate. In the next step carbonyl oxygen atom interacts with the carbon atom of the epoxide cycle without rupture of the imide cycle that reduce to the formation of trans-dihydroxiimide (**II**) product. The energy barriers calculated for the second step of the process are much higher than those for the first step.

The transformations of epoxyimide which involve ring-opening process (with possible proton migration from the hydroxyl group in the hydrolysis to the nitrogen or oxygen atom of imide) with subsequent lactonization reaction were found less favorable.

Structural Studies on Alkyl-Substituted Polysilane Derivatives in solutions

I.V. Korotkova, Yu.E. Sakhno, I.K. Drobit'ko, T.V.Sakhno

Academy of Sciences of Technological Cybernetics of the Ukraine

The role of molecular modelling in spectroscopy is great enough, despite of an obvious priority of experimental researches in this area. Such theoretical results which cannot or be received extremely difficultly experimental methods are most significant. Among theoretically studied materials, organopolysilanes (poly(di-n-alkylsilanes)(PDAS) and poly(di-n-hexylsilanes)(PDHS)) are linear high polymers composed of a chain of silicon atoms *a* bonded together, with two organic substituents attached to each backbone silicon. Major progress over the past decade in the characterization of these materials has led to an increased recognition of their potential technological applications as silicon carbide precursors, as photoconductors, as the top agenda of many polymer chemists and physicists. Most of these technological applications depend intimately on the electronic structure and resulting spectral properties of these materials. Although many structural and electronic questions have been resolved for PDAS and PDHS, the difference between the position of the UV absorption maximum in solution at low temperature and the crystalline polymer remains unanswered.

In connection with that studied molecular systems are used in fluid and solid solutions where their absorption spectra effects by solvent polarity the development of methods of aprioristic-structural modelling of influence of the specified factors within the limits of quantum-chemical methods that will allow to carry out purposeful search of effective molecular systems is actual. Comparison of experimental and computation values of electronic structure of molecules on ground and excited state, and also at change of geometry of separate fragments, will yield the necessary information for selection of effective molecular systems at the decision of applied problems.

The calculations were carried out in the approaches of PM3 (HyperChem 7.0) and ab anitio TD/CEP-31G (Gaussian 98). Geometries of all molecules were optimized at the semi-empirical level of the theory using PM3 Hamiltonian using HyperChem 7.0 computational package. On the basis of these geometries, the transition energies and the oscillator strengths were calculated with configuration interaction wave functions, where all electronic states were included which are generated by singly exciting all electrons in the 14 highest occupied MO to the 14 lowest unoccupied MO with respect to the ground state.

By the computation results we discussed effects of solvent polarity on electronic characteristics of polymers. Inter-dependencies of rotations between adjacent side chains as well as between backbone and side-chain rotations were examined. The dependence of energy levels electronic-excited states of investigated compounds are analyses as a function of the Si-Si and Si-C torsion angle. The points were selected at intervals of 5^0 for twist angle ranging from 0^0 – 90^0. Some conclusion concerning correlation solvent polarity and electronic structure of the studied systems were made and possibilities of their application were discussed.

A quantum chemical study on the reactivity of some azo-compounds and relative triazenes in aqueous and organic solutions

I.M. Maga

Uzhgorod Border State Control and Toxicological Laboratory, Stanciyna Str. 56, Uzhgorod 88000, Ukraine; e-mail: updktl@mail.uzhgorod.ua

Calculations have been carried out on the equilibrium geometry of some triazenes (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) as well as their isomer forms differing by H atom position by means of ab initio Hartree-Fock-Roothaan method using simplest valence-split 3-21G** basis set. The iso forms appeared to be more stable in gas phase.

Various complexes of triazene molecules with solvent molecules were examined. Differences between energy values of usual and iso-forms seem to increase when intermolecular complexes with polar solvent molecules are formed. In particular, water molecules and those of acetonitryle or formamide were tested. When treated within the frameworks of the continual PCM model, these structures performed an analogous behavior.

A mechanism is proposed of transformations between usual and iso-forms of triazenes in aqueous medium suggesting a sinchronic exchange of hydrogen atoms between triazene and water molecules. This idea is rather close to that described in the work [1].

Spatial structures and energy characteristics were found also for molecules of azo-compounds (p-H_2N-C_6H_3(R)-N=N-C_6H_4-NO_2, where R = H, o- and p-CH_3). Probable compositions of solvate complexes between these compounds and solvent molecukes were also considered. The primary hydrate cover of azocompound molecules was shown to consist of six water molecules. The effect was also examined of the number of solvent molecules and their geometry on the stability of the complexes.

Electron absorption spectra of azo-compounds and triazenes were calculated within the frameworks of configuration interactions method. Spectral shifts were found caused by the effect of solvents.

[1] Fdez Galván I., Aguilar M.A., Ruiz-López M.F. Theoretical study of the 1,3-hydrogen shift of triazene in water // *J. Phys. Chem.* B **109** (48) (2005) 23024-23030.

Ab initio modeling of K, Mg asparaginate in water solution with various acidity

V.S. Soldatov, A.L. Pushkarchuk, Z.I. Kuvaeva

Institute of Physical – Organic Chemistry NASB, 220072 Surganova, 13 Minsk, Belarus

The Potassium and Magnesium Asparaginates ($(Asp^{-})_3\ K^{+}\ Mg^{2+}$) is the active component of a medical product which known as Asparcam (Belarus, Ukraine, Russia), Panangin® (Gedeon Richter, Hungary), Pamaton® (PHARMACIA AD), "Potassium-magnesium asparaginate" (Berlin-Chemie). This medicine is widely used as an effective remedy which has an influence on metabolic processes.

At peroral administration the Asparcam is dissolved in water solutions with various acidities (from strong acid medium in a stomach up to weak base medium in bowels).

Being the mixed salt of a weak acid it can exist either as independent separate molecules, or as stable ionic associate. The information on changes of $(Asp^{-})_3\ K^{+}\ Mg^{2+}$ structure with changing of its concentration of the water solution is important both for establishing of mechanisms of their medicinal action and for development of more effective ways and techniques for application of appropriate medicinal agents. Up to now this question is not investigated. To receive this information, the systematic theoretical study of atomic structure of various models of compounds containing $(Asp^{-})_3\ K^{+}\ Mg^{2+}$ has been done.

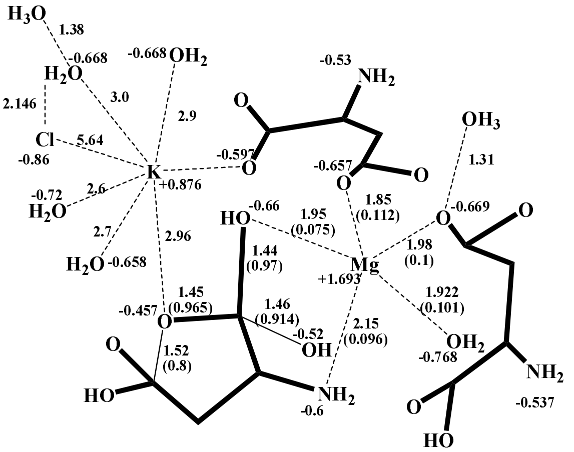


Fig.1. Structural formula of supermolecule $(Asp^{-})_3\ K^{+}\ Mg^{2+} + 100H_2O + 1HCl$, charges on atoms in a.u., bond lengths in Å and bond orders (in brackets) in a.u.

In continuation to our previous paper [1] we present here the results of *ab initio* quantum-chemical studies of structure and stability of $(Asp^{-})_3\ K^{+}\ Mg^{2+}$ in water solutions in the presence of HCl molecules applying of supermolecule model. The supermolecules holding $(Asp^{-})_3\ K^{+}\ Mg^{2+} + nH_2O + mHCl$ ($n = 20, 40, 60, 100$; $m= 1,2$) have been calculated. The charge distribution and bond characteristics (bond lengths and bond orders) were received.

In all cases the structures were optimized by using the total energy minimization of the system. The structural formula of $(Asp^{-})_3\ K^{+}\ Mg^{2+} + 100H_2O + 1HCl$ supermolecule after full geometry optimization is shown in Fig. 1.

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

The calculations were performed using the MINI basis. The software package PC GAMESS [2] based on GAMESS (US) [3] was used.

This work was supported by Belarusian Republican Foundation for Fundamental Research (grant X07-284)

[1] Soldatov V.S., Pushkarchuk A.L., Kuvaeva Z.I. *MACC-1 Book of abstracts*; Kharkiv, 30 June- 1 Jule 2005, p. 71.

[2] Granovsky Alex., www http://classic.chem.msu.su/gran/gamess/index.html

[3] Schmidt M.W. et. al., *J.Comput.Chem.* **14** (1993) 1347.

Comparison of PLS and decision trees methods by the example of solution QSAR task for ligands of 5-HT$_{1A}$ receptors

P.G. Polishchuk, V.E. Kuz'min, A.G. Artemenko, A.I. Khromov

A.V.Bogatsky Physico-Chemical Institute of the National Academy of Sciences of Ukraine, 86 Lustdorfskaya doroga, Odessa 65080, Ukraine; E-mail: pavel_polischuk@ukr.net

Very often researchers have to deal with ranking observations of investigated property (activity). In this case using of regression methods of analysis becomes inappropriate. Using of the decision trees method is very suitable in such situation. But it was used very rarely in solutions of QSAR tasks due to difficulties of quantitative interpretation of its models. A new approach to solve this problem was proposed. It is based on the procedure of trend-vector method and can be describe by the following formula:

$$T_j = \frac{I_j}{m}\sum_{i=1}^{m}\left[\left(A_i - A_{mean}\right)\right]$$

where T$_j$ – relative influence of j-th descriptor, I$_j$ – improvement, coefficient that shows splitting effectiveness in decision trees model by j-th descriptor, m – number of compounds in this node, A$_i$ – affinity rank of i-th compound, A$_{mean}$ – mean affinity rank for whole work set.

Applying this procedure to each node of resulting decision trees model can allow estimating the relative influence of each descriptor used in the model. Moreover, each descriptor relative influence (T$_j$) has a corresponding range of descriptor value, inside which this influence is implemented.

Proposed approach was tested in the solution of QSAR task for 316 ligands of 5-HT$_{1A}$ receptors. Simplex representation of molecular structure was used which can simplify of model interpretation. SPSS Answer Tree 3.0 (trial version) and C&RT (Classification and Regression Trees) algorithm were used for construction of decision trees model. The final model selected 44 simplex descriptors from whole set of them. According to described procedure relative influences were calculated in each of 157 nodes of the obtained model. Finally, using of simplex descriptors allowed us to select molecular fragments which had steady influence on the affinity of ligands of 5-HT$_{1A}$ receptors.

At the same time this task was solved by partial least squares (PLS) method and steady influenced molecular fragments were chosen too. The obtaining results were in accordance with each other that can be a proof of adaptability of the proposed approach of the decision trees models interpretation.

New structural descriptors of molecules on the basis of symbiosis of the informational field model and simplex representation of compounds. QSAR analysis of luminescent properties of derivatives of 2-oxo-4-hydroxy-quinolin-3-carboxylic acid

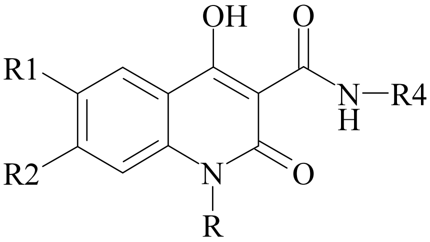
L.N. Ognichenko, V.E. Kuz'min, A.G. Artemenko, V.P. Antonovich,
A.V. Yegorova, D.I. Alexandrova

A.V.Bogatsky Physico-Chemical Institute of the National Academy of Sciences of Ukraine, 86 Lustdorfskaya doroga, Odessa 65080, Ukraine; e-mail: ognichenko@mail.ru

In the given work, the scheme of calculation of new structural parameters is offered on the basis of symbiosis of the informational field model [1] and simplex presentation of molecular structure [2]. Such structural characteristics can be used for the solution of the different QSAR tasks.

From a formal position the model of the potential informational field for any object describes a situation where the surrounding space is structurized by the object, i.e. the object generates the potential information in this area. The information field of complex object can be modeled as a superposition of the appropriate fields of its independent parts (elements). In the framework of the information field model every atom depends on influencing of all other atoms of given molecule. Character of such influencing depends on atom properties, fixed in basis of construction of informational field and mutual position of atoms in molecule. In a result of analysis of the different model systems it was found out some peculiarities determined by atom nature and geometry of molecule on the whole for mutual influencing of atoms.

In the simplex representation of molecular structure a molecule is represented as the system of different simplex descriptors (tetratomic fragments with fixed composition, structure, chirality and symmetry). In the given approach it is offered to differentiate atoms in simplex on the basis of the informational field characteristics, which are calculated in points of the atom location. It is noteworthy that it is possible to use potentials of the informational fields, weighed by different atomic properties (charge, lipophilicity, refraction etc.). In fact, such field reflects information about the distribution of the considered property in space.



Thus, the given approach enables to generate the set of new structural descriptors, reflecting information about the peculiarities of molecular structure. The efficiency of method was demonstrated on the example of analysis of structure influence of 2-oxo-4-hydroxy-quinoline-3-carboxylic acid derivatives on the luminescent properties of ions of Eu $^{(III)}$ and Tb $^{(III)}$ complexes. QSAR task has been solved using PLS-method because this method is more acceptable than MLR when the large number of structural parameters was used. Statistic characteristics for obtained 2D models are satisfactory (R^2=0.978-0.997, leave-one-out cross-validated Q^2=0.917-0.986). 2D models contain information about structure of compound and reflect only the topology of the molecule. The capacity of such approach is that the topology model of molecular structure in an implicit kind contains information about possible conformations of the compound. On the basis of the received models the structural fragments with the maximal influence on luminescent quantum yield and lifetime have been defined. Within the framework of given approach it is possible to define the relative influence of the different factors on the luminescent properties of complexes of ions of Eu $^{(III)}$ and Tb $^{(III)}$.

[1] Kuz'min V.E., Ognichenko L.N., Artemenko A.G. Modeling of the informational field of molecules // *J.Mol.Mod.* **7** (7) (2001) 278 – 285.

[2] V.E. Kuz'min, A.G. Artemenko, P.G. Polischuk, E.N. Muratov, et al. Hierarchic System of QSAR Models (1D-4D) on the Base of Simplex Representation of Molecular Structure // *J. Mol. Model.* **11** (2005) 457 - 467.

Research of circular models efficiency for QSAR tasks

A.V. Liahovskiy, V.E. Kuz'min, A.G. Artemenko

A.V.Bogatsky Physico-Chemical Institute of the National Academy of Sciences of Ukraine, 86 Lustdorfskaya doroga, Odessa 65080, Ukraine; E-mail: 1dqsar@rambler.ru

In the present time QSAR analysis is important part of development of new compounds with complex of desired properties. Used QSAR methods differ from each other with way of generation of descriptors, levels of detailing of molecular structure and the algorithms of the mathematical description.

The purpose of this work is elaboration of the new method of generation of descriptors based on the circular description of molecular structure. Earlier the method based on using of structural parameters with characteristics received from the harmonic analysis of torsions angles have been offered for the description and estimations of structural similarity of cyclic structures [1].

For distribution of the similar approach on any structures the algorithm of the unified description of non-cyclic structures using parameters of pseudo-cycle is offered.

For this purpose the structure is represented as a molecular graph. For the molecular graph we solve traveling salesman problem by branch and bounds method [2]. Investigated molecular graph is represented by matrix of costs (the minimal distances between graph vertexes). As a result of the problem decision we received a pseudo-cycle that represents an initial sequence of atoms' numbers of the investigated molecule. Calculation of physical and chemical characteristics of atoms along a pseudo-cycle gives molecular spectrum. Harmonic analysis (Fourier-transform) of this molecular spectrum gives parameters for QSAR analysis.

For the estimation of efficiency of the developed QSAR approach the ability to angiotensin converting enzyme (ACE) inhibition (pIC_{50}) has been investigated [3]. Training set consists of 76 compounds and 38 structures were used in a test set. It is necessary to note that all investigated compounds are structurally homogeneous that facilitates the procedure of molecules superposition in lattice methods.

We have compare in the given work the resulting PLS-models [4] built with the use of descriptors generated in the followings QSAR approaches:

a) CoMFA – Comparative Molecular Fields Analysis; b) CoMSIA – Comparative Molecular Similarity Indexes Analysis; c) EVA – Eigenvalue Analysis; d) HQSAR – Hologram QSAR; e) Cerius 2 program package – method of traditional integral (whole-molecule) 2D and 2.5D descriptors generation.

The advantage of the developed by us method over others has been revealed by the comparison of such statistical descriptions of QSAR models as determination coefficient for training (R^2) and test (R^2_{test}) sets; determination coefficient calculated in the cross-validation terms (Q^2); as well as the standard errors of prediction for both sets. For example for Circular model Q^2= 0.86-0.91, and for the other methods Q^2 = 0.66-0.72. Moreover, Circular models allowing determining structural fragments with positive or negative influence on investigated property as well as the contribution of different physical-chemical factors in the activity changes.

[1] D. Cremer, J.A. Pople. A General Definition of Ring Puckering Coordinates // *J. Am. Chem.Soc.* **67** (1975) 54-57.

[2] Land A.H, Doig A.G. An autmatic method of solving discrete programming problems// *Econometrica* **28** (1960) 497-520.

[3] J.Sutherland, J O'Brien, L.A Weaver. A comparison of methods for modeling quantitative structure-activity relationships.// *J. Med. Chem.* **47** (2004) 5541-5554.

[4] Rännar S., Lindgren F., Geladi P., Wold S. A PLS Kernel Algorithm for Data Sets with Many Variables and Fewer objects. Part 1: Theory and Algorithm. // *Journal of Chemometrics* **8** (1994) 111-125.

Competition between intra and intermolecular hydrogen bonding in the resorcinarene tetrabenzoates

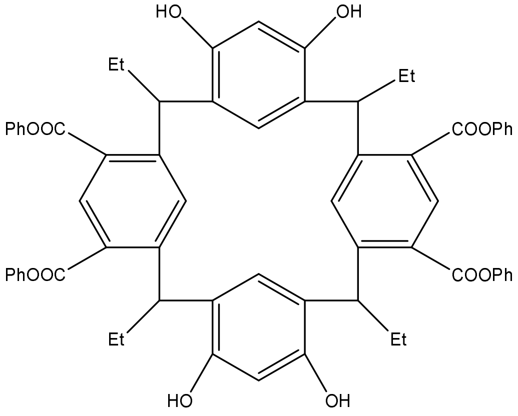
S.V. Shishkina[a], O.V. Shishkin[a], A.V. Shivanyuk[b], V.I. Kalchenko[b]

[a]STC "Institute for Single Crystals", National Academy of Science of Ukraine, 60 Lenina ave., Kharkiv 61001, Ukraine, E-mail: sveta@xray.isc.kharkov.com

[b]Institute of Organic Chemistry, National Academy of Sciences of Ukraine, Kyiv-94, 02660, Murmanska str. 5, Ukraine

Calixarenes represent perspective class of organic compounds for the modeling of the molecular identification processes and for the investigation of the molecular and ionic transfer through cellular membrane processes etc. Presence in aromatic rings of calixarene proton donating and withdrawal substituents creates suitable conditions for formation of intramolecular hydrogen bonds. However, in crystal phase it is possible to obsreve competition between intra and intermolecular hydrogen bonding. Presence of solvents molecules promotes such competitions and it may lead to switch between intra and intramolecular hydrogen bonds.

The results of the X-ray diffraction study of the molecule **1,** which exist in the crystal phase as solvate with acetonitrile, demonstrates that the intra- or intermolecular C=O…H-O hydrogen bonds are not formed. All OH groups form the intermolecular hydrogen bonds with acetonitrile molecules.



1

The results of the quantum-chemical calculations by B3LYP/cc-pvdz method demonstrated that the formation of the intramolecular hydrogen bonds between hydroxyl and carboxyl group in non-solvated molecule **1** leads to the decrease in energy on 7.48 kcal/mol (as compared with molecule **1** without intramolecular hydrogen bonds). In the presence of the acetonitrile solvent the formation of the O-H…N intermolecular hydrogen bonds is more energy favorably (on 7.28 kcal/mol) in comparison with the O-H…O=C intramolecular hydrogen bonds.

The nature of intermolecular interactions in crystals of polynitro compounds

I. V. Fedyanin, M. Yu. Antipin, K. A. Lyssenko

A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 119991Vaviova st. 28, Moscow, Russian Federation

The nature of shortened contacts in crystals of nitramines (N-methylnirtamine, MNA; hexanitrohexa-azaisowurtzitane, CL-20, hexanitrohexaazaisowurtzitane, RDX), nitroarenes (1,3,5-trinitrobenzene, TNB; 1,3,5-trinitroaniline, TNA) was analyzed on the basis of the high-resolution X-ray investigation. The topological analysis within the Bader's "Atom in molecules" theory was used to find all attractive intermolecular interactions and estimate their energy using an empirical correlation between the potential energy density an the energy of the contact. Lattice energies obtained as a sum of contact energies are in good agreement with the thermochemical data. The dependence of number and energy of predominant-type interaction on the compound structure was demonstrated. Lattice energy was also calculated using PW-DFT approach in solid.

Two independent molecules (A and B) in the crystal of TNB were analyzed. It was shown that these molecules differ not only in symmetry and molecular conformation, but also in number of contacts, charge and molecular volume. Analysis of intermolecular contacts revealed the anisotropy of contacts distribution what was proved by the X-ray investigations at different temperatures.

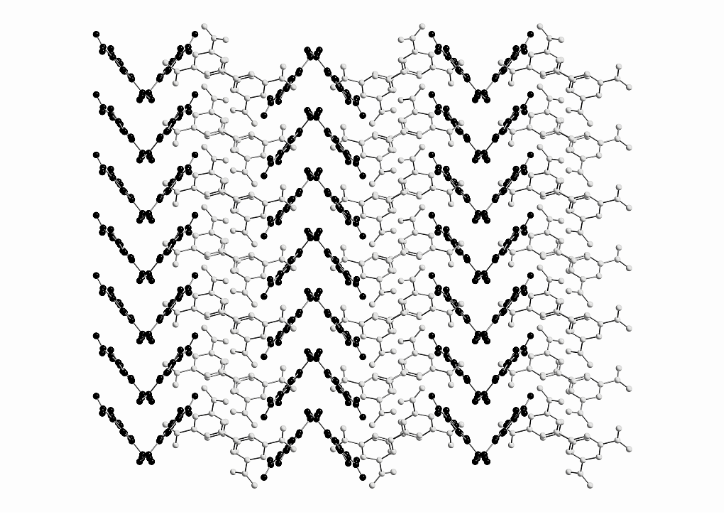


Fig. 1 The alternation of layers formed by "A" and "B" independent molecules in crystal of TNB

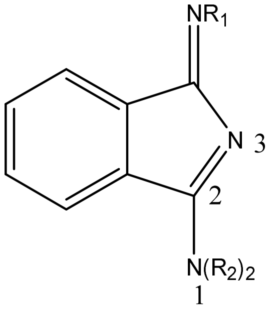
This work is supported by RFBR 06-03-32557.

Crystal packing induced polarization of the electron density in aminoiminoizoindoles

I.S. Konovalova[a], R.I. Zubatyuk[a], S.V. Shishkina[a], O.V. Hordienko[b],
M. Yu. Kornilov[b], O.V. Shishkin[a]

[a] ***STC "Institute for Single Crystals" NAS of Ukraine, 60 Lenina ave., Kharkiv, Ukraine***
[b] ***Taras Shevchenko National University, 64 Volodymyrs'ka st., Kyiv 01033, Ukraine***
E-mail: irinak@xray.isc.kharkov.com

It is known, what the aminoiminoizoindole is a structural fragment of the porphyrins. This causes interest to structure and properties of these compounds.



где R_1-H,1,2,4-Trimethyl-benzene, 1-Methyl-3-nitro-benzene, 1-*p*-Tolyl-ethanone.
R_2- H, methyl, ethyl.

Scheme 1 – the investigated objects

The X-ray diffraction study of series of the aminoiminoizoindole derivatives (scheme 1), reveals interesting features of structure of the NR_2-C=N fragment. It is demonstrated that the C1-N2 bond is considerably shorter, and the C2-N3 bond is longer as compared to average values for single and double C-N bonds.

The results of the quantum-chemical calculations using B3LYP and MP2 methods with aug-cc-pvdz basis set demonstrate that in isolated molecules values of the bond distances are close to their average bond lengths. Therefore, significant electron density redistribution in the crystal phase cannot be caused by intramolecular interactions and should be associated with crystal packing effects.

Application of Polarizable Continuum Model (PCM) with DFT calculations for modeling of environment influence results in considerable change of bond lengths within the NR_2-C=N fragment toward values found in the crystal phase. Thus, it can assume, that the delocalization of the electronic density in the aminoiminoizoindole and its derivatives causes by the polarizing influence of the neighboring molecules in the solid state.

DFT modeling of ESR parameters of nanodiamonds with single $[NV]^-$ center

V.A. Pushkarchuk[a], S.Ya. Kilin[b], A.P. Nizovtsev[b], V.E. Borisenko[a],
A.B. Filonov[a], A.L. Pushkarchuk[c], S.A. Kuten[d]

[a]Belarusian State University of Informatics and Radioelectronics, P. Brovka 6, 220013 Minsk, Belarus

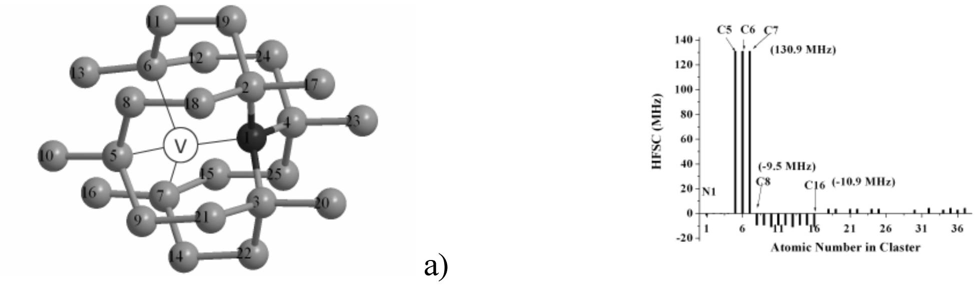
[b]Institute of Physics NASB, Nezavisimosti Ave. 68, 220072 Minsk, Belarus.

[c]Institute of Physical – Organic Chemistry NASB, Surganova, 13 220072 Minsk, Belarus, alexp51@bk.ru

[d]Institute for Nuclear Problems, Belarusian State University, Minsk, Belarus

The $[NV]^-$ centers in diamond which consists of substitutional N atom and vacancy (V) in the nearest site of lattice are considered nowadays as great-potential candidate system for implementations of many quantum-optical devices (quantum computer, single photon emitter, etc.) and undergo extensive studies both experimentally and theoretically [1,2].

In continuation to our previous paper [3] here we present the results of systematic theoretical studies of atomic configurations, electronic and spin properties of various diamond nanoclusters with single $[NV]^-$-center obtained by *ab initio* DFT quantum-chemical method. The hydrogen-passivated diamond nanoclusters $C_{27}H_{36}[NV]^-$, $C_{33}H_{36}[NV]^-$, $C_{36}H_{42}[NV]^-$ were considered. The isotropic and anisotropic hyperfine splitting constants (HFSC) of ^{14}N and ^{13}C in nanoclusters were calculated. The example of calculated isotropic HFSC for N and various C atoms in $C_{36}H_{42}[NV]^-$ cluster is presented in Fig. 1.



a)

b)

Figure 1. a) The atomic numeration of the first and second coordination spheres to the vacancy in $C_{36}H_{42}[NV]^-$ cluster; b) Isotropic HFSC for N and C atoms in the $C_{36}H_{42}[NV]^-$ cluster.

The isotropic HFSC have their maximum values at C_5, C_6 and C_7 atoms being nearest neighbors to the vacancy, which vary in range of 130-170 MHz depending on the basis set, cluster's size and shape. These results are in good quantitative agreement with the experimental data of electron spin resonance (ESR) for $[NV]^-$-center in bulk diamond (130 MHz). The isotropic HFSC values of the second vacancy's neighbors (C_8-C_{16}) are more than order of magnitude smaller than for the first ones. The calculations were performed with the B3LYP1 functional and MINI/EPRII basis. The software package PC GAMESS [4] based on GAMESS (US) [5] was used.

This work was supported by INTAS, grant N 04-77-7289 and EU (FP6 STREP "EQUIND"), Contract N 034368.

[1] Wrachtrup J., Kilin S.Ya., Nizovtsev A.P. *Optics & Spectroscopy* **91** (2001) 429.
[2] Wrachtrup J., Jelezko F. *J. Phys.: Cond. Matter.* **18** (2006) S807.
[3] Pushkarchuk V.A. et. al., *Optics & Spectroscopy* **99** (2005) 245
[4] Granovsky Alex., www http://classic.chem.msu.su/gran/gamess/index.html
[5] Schmidt M.W. et. al., *J.Comput.Chem.* **14** (1993) 1347.

DFT modeling of spin parameters of nanosilicon doped by Al and P atoms as single impurities

A.L. Pushkarchuk[a], S.Ya. Kilin[b], A.P. Nizovtsev[b], V.A. Pushkarchuk[c],
S.A. Kuten[d], T.N. Mamedov[e]

[a]Institute of Physical – Organic Chemistry NASB, Surganova, 13 220072 Minsk, Belarus, alexp51@bk.ru

[b]Institute of Physics NASB, Nezavisimosti Ave. 68, 220072 Minsk, Belarus.

[c]Belarusian State University of Informatics and Radioelectronics, P. Brovka 6, 220013 Minsk, Belarus

[d]Institute for Nuclear Problems, Belarusian State University, Minsk, Belarus

[e]Joint Institute for Nuclear Research, 141980 Dubna, Moscow region, Russia

Electron and nuclear spins of impurity centers like ^{31}P, Al and ^{29}Si in silicon are considered now as possible candidates for physical carriers of qubits in practical implementations of solid-state quantum computer processor (see, e.g., [1,2,3]) owing to its potential compatibility with well-developed modern silicon-based microelectronics. Recently, the measurement of spin state and the observation of Rabi flops of ^{31}P donor electrons in silicon by purely electric means have been demonstrated [4]. Therefore, quantum-chemical analysis of these perspective systems is of great interest.

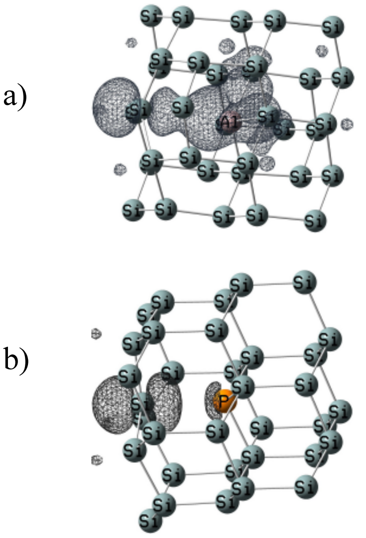


Fig.1. Spatial spin density distributions in a) $Si_{34}H_{36}$[Al] and b) $Si_{34}H_{36}$[P] clusters. The H atoms are not shown.

Here we present the results of systematic theoretical studies of atomic configurations, electronic and spin proper-ties of various silicon nanoclusters with single Al and P atoms ([Al or P]) as impurities, obtained by DFT quantum-chemical method. The hydrogen-passivated silicon nano-clusters $Si_{28}H_{36}$[Al, P], $Si_{34}H_{36}$[Al, P], $Si_{70}H_{84}$[Al, P] are considered. Spatial spin density distribution and isotropic and anisotropic hyperfine splitting constants (HFSC) at Al, P and Si atoms in nanoclusters are calculated. The examples of calculated spatial spin density distribution in $Si_{34}H_{36}$[Al] and $Si_{34}H_{36}$[P] clusters are presented in Fig. 1.

The spatial spin density and isotropic HFSC for $Si_{34}H_{36}$[Al] cluster have their maximum values at Si neighbors atoms and at Al atom (Fig1a). The spatial spin density for $Si_{34}H_{36}$[P] cluster have their maximum values at P atom and neighbor Si atom (Fig1b). The calculations were performed with the B3LYP1 functional and MINI basis. The software package PC GAMESS [2] based on GAMESS (US) [3] was used.

This work was supported by NSF of Belarus under grant Ф06-323.

[1] Kane B.E. *Nature* **393** (1998) 133; *Fort. Phys.* **48** (2000) 1023.
[2] Baturin A.S., Gorelkin V.N., Singh R. *Optics and Spectroscopy* **94**(6) (2003) 895.
[3] Itoh K.M. *Solid State Communs.* **133** (2005) 747.
[4] Stegner A.R., et. al. *Nature Physics* **2** (2006) 835.
[5] Granovsky Alex., www http://classic.chem.msu.su/gran/gamess/index.html
[6] Schmidt M.W. et. al., *J.Comput.Chem.* **14** (1993) 1347.

Quantum-chemical investigation of the nature of phase transition in the $Sn_2P_2S_6$ ferroelectrics

O.I. Chobal, I.M. Rizak[a] and V.M. Rizak

[a]***Dnipropetrovsk National University, Dnipropetrovs'k, Ukraine***
Uzhgorod National University, Uzhgorod, Ukraine
E-mail: rizak@univ.uzhgorod.ua

The topic character of studies of the $Sn_2P_2S_6$ crystals is due to the promising character of their practical application as the primary pyro- and piezotransformers in a wide temperature range. At the same time, interpretation of the available results of studies gives no unambiguous answer to the question concerning the type of ferroelectric phase transition in the $Sn_2P_2S_6$ crystals. Modeling of the lattice instability within the framework of the quasi-molecular cluster method could be an essential addition to the pattern of the phase transition in the crystals under study. Therefore the goal of this work was to study the nature of the phase transition in the $Sn_2P_2S_6$ crystals.

In this work we present the results of direct non-empirical calculations of the form of a local adiabatic potential and corresponding force constants for Sn atoms, which are displaced at phase transition. Local adiabatic potentials for Sn atoms are studied using total energy calculations by *ab initio* Hartree-Fock (RHF) method for many-atomic clusters $Sn_8P_8S_{24}$ and $Sn_{30}P_{30}S_{90}$. The $Sn_8P_8S_{24}$ cluster was used for calculations since it is the minimal cluster, which reproduces the chemical bonding and the local (i.e. determined by this bonding) properties. All calculations have been carried out by means of the PC GAMESS code of the GAMESS (US) quantum-chemical software using the basis set 3-21++G**.

Calculated local potential for the Sn atom has a form of a single-well potential that allows ferroelectric phase transition in the $Sn_2P_2S_6$ crystals to be classified as the displacement-type phase transition. The effect of the sizes of clusters on a shape of the local potential for the central Sn atom is considered.

The Singlet Oxygen Activation by Unique Metal Ion Structures in Zn(2+)/ZSM-5 Zeolite: DFT study of the Adducts of Activated Singlet Oxygen with Propene or Propyne

Vitaly Solkan

N. D. Zelinsky Institute of Organic Chemistry, RAS, 119991 Moscow, Leninskii pr. 47, Russian Federation; E-mail: solkanvn@ioc.ac.ru

The participation of singlet oxygen in the oxidation of hydrocarbons on heterogeneous catalysts was discussed previously. Recently, the first direct evidence of the non-equilibrium thermal production of $^1\Delta_gO_2$ on zeolite samples (ZSM-5 exchanged with alkaline and alkalin-earth cations) was obtained by chemiluminescence technique [1]. We present herein a density functional theory (DFT/B3LYP) study on the interaction of molecular oxygen with Zn(2+) ($3d^{10}$), exchanged zeolite ZSM-5. The cation-exchanged sites in ZSM-5 are represented by a variety of model clusters, including 3T, 10T, and 6T-ring (7T cluster) (T denoted tetrahedral Al and Si atoms). The six-membered ring 6T-ring (7T cluster) composed of two five-membered rings from the walls of the straight channels of the ZSM-5 zeolite was selected since it has been discussed by experimentalists. Hydrogen atoms were used to saturate the dangling Si–O bonds at the periphery of the clusters. The starting geometry of the clusters corresponded to the real lattice of the ZSM-5 zeolite corresponding to X-ray diffraction data. Natural bond orbital (NBO) population analysis was carried out on the optimized structures to determine the occupancies (number of electrons assigned to orbitals in each atom) and charges of atoms in the adsorption complexes. Analytical frequencies were calculated at the same level of theory, and the nature of the stationary points was determined in each case according to the number of the negative eigenvalues of the Hessian matrix. The theoretical calculations using 3T, 10T, and 7T clusters show that oxygen adsorption by Zn(2+)-ZSM-5 results in a very strong perturbation of O–O stretching vibration. This correlates with the finding that the O-O/Zn bond length is much longer than O-O bond length for free $^1\Delta_gO_2$ molecule. In order to elucidate the reactivity of singlet oxygen on Zn(2+) site in ZSM-5 we will focus on calculations using 3T and 7T cluster at DFT/B3LYP/6-31G(d, p) level. We have investigated the reaction of singlet oxygen with double-bond compounds (propene and butadiene) to give a dioxetane intermediate, which usually cleaves to aldehydes. The activated oxygen molecule on Zn(2+)/ZSM-5, as a one-electron acceptor, binds strongly to the propene molecule, resulting in formation of dioxetane adduct, namely 3-methyl-1,2-dioxetane. Due to the electron withdrawing effect, electron transfer from the propene molecule occurs and inducing subsequent stronger binding of the molecular oxygen to propene. The changes in the geometrical parameters, charge distribution and dipole moment along the reaction coordinate are discussed. Some relationships between the amount of transferred electron density and the changes in geometrical parameters and energies are given. These results indicate that the activated singlet oxygen on Zn(2+)/ZSM-5 may initially oxidize propene to dioxetane adduct, which seem to play an important role for the propene oxidation. Quantum chemical calculations indicated that for butadiene both the six-membered and four-membered cyclic peroxides have been formed from oxygenation reaction that involve singlet oxygen adsorbed on Zn-3T-cluster. The former reaction (2+4)-cyclo-ethylene-1/4-addition is actually a Diels-Alder reaction with singlet oxygen as dienophile. Carbon-carbon triple bonds can also undergo 2+2-cycloaddition with activated singlet oxygen. Computed thermodynamic data of the 2+2-cycloaddition reaction of singlet oxygen with propyne indicate that this process is exothermic. The product geometry corresponds to a 3-methyl-1, 2-dioxete molecule. Theoretical results obtained employing DFT method provide a mechanism of propene and propyne oxidation based on electronic effects responsible for selective reactivity of singlet oxygen adsorbed on Zn(2+)-site in ZSM-5 zeolite. Financial support of this research by RFBR (project 05-03-33103) is gratefully acknowledged.

[1] A. N. Romanov, Y. N. Rufov, and V.N. Korchack, *Mendeleev Commun.* (2000) 117.

Mesoporous silica MCM-41 and intercalation compound with PDHS

V. Khavryuchenko [a], N. Ostapenko [b]

[a] ***Institute for Sorption & Endoecology, National Academy of Sciences of Ukraine, Gen. Naumova str.13, 03680 Kiev, Ukraine; email: vkhavr@compchem.kiev.ua***

[b] ***Institute of Physics, National Academy of Sciences of Ukraine, pr. Nauky 46, 03680, Kiev, Ukraine, e-mail: ostap@iop.kiev.ua***

The atomic-level model of the mesoporous silica MSM-41 was developed. Quantum chemical calculation (semiempirical method PM3) with complete space structure optimization was done for the cluster with total amount of atoms 1728. Hydroxyl groups saturated the cluster bond ends, which represents the real properties of the nanosilica systems. The pore diameter of the hexagon hole is 27 Å approximately. Inside surface of the hexagon hole is hydroxyl-free. The hydroxyl-groups can exist only on the defects and at the hole end. A series of the different length polysilane with different terminating groups: hydrogen, methyl and hexyl. For hydrogen and methyl groups the amount of silicon atoms were from 2 up to 100 and for hexyl groups up to 20. For biggest oligomer total amount of atoms is 818. The electronic structure and HOMO, LUMO and GAP position for all systems were analyzed. For the silicon linear chains with length more that 20 silicon atoms the position of HOMO, LUMO and GAP are approximately constant. The most stable conformation for the silicon linear chain is trans. Hexyl derivatives polysilane (PDHS) has an approximately diameter in 18 Å. The diameter for the PDHS molecule is defined as distance between hydrogen atoms for the end methyl groups, which placed on the end of hexyl groups, and belong to the neighbour silicon atoms. These data show that this polymer is able to penetrate into the MSM-41 holes.

Intercalation composite for the MSM-41 silica and PDHS polymer was simulated using quantum chemistry in cluster approximation, too. Total amount of the atoms in this cluster is 2546 and characteristic size of this system is around 40 Å. Computation data show that PDHS molecule can exist in the MSM-41 hole only in trans-conformations. Space and electronic properties for this big cluster is compared and discussed respect to the ‘free’ molecules. Additionally some possible defects in the MSM-41 silica like insight hydroxyl groups and silicon atom vacancies were simulated, too. A set of the silica clusters with different hole diameter was simulated and ability to some PDHS molecule penetration in the same hole was analyzed. Results of the computer simulation were compared with experimental spectroscopic data. The bigger silica clusters with pore diameter near 60 A and with length near 80 A were simulated, too. Total amount of atoms in this system under study is 8964. The pore size of this cluster can hold more then one PDHS molecules. We have tested three PDHS molecules, every of which contains 818atoms, and these three molecules, in trans-conformation only, occupy three corners in the hexahedron pore of the cluster. Total amount of atoms in this system is 11418. The cluster’s size and total amout of atoms may reproduce the structure and packing method for big size organic polymers in the meso-scale pores. Depends on the size, this pore can contain the different amount of polymer chain(s), but only in the trans-conformation. Conformation changing leads to the big ball formation, which cannot penetrate inside the pore.

Quantum chemical simulation of intermolecular interaction of bubble silica molecules with hydroxyl groups

O.V. Polischuk, V.V. Lobanov

A.A. Chuiko Institute of Surface Chemistry of National Academy of Sciences, Gen. Naumov Street 17, 03164 Kyiv, Ukraine

E-mail: polischuk_ov@mail.ru

The fields of science and technology connected with preparation and application of crystalline and amorphous silica forms are of great interest nowadays. The problem of production of new materials on the basis of this silica forms is especially actual now.

The matter properties essentially change, when transiting from macrostructures to nanosize ones. Therefore the examination of silica nanoparticles and derived systems increasingly draws attention of scientists. Silica nanoparticles should have new important properties different from those of bulk silica similarly to fullerenes and carbon nanotubes.

In previous works we examined theoretically structural and energy characteristics of two fundamental different bubble silica molecules. The former is a $(SiO_2)_N(H_2O)_{N/2}$ molecule which characterized by availability of hydroxyl groups at each silicon atom. These groups are oriented out of spherical cage. The latter is a fully coordinated molecule $(SiO_2)_N$ with ideal for silica stoichiometry of 1:2. The calculations have been carried out by means of density-functional theory method, the B3LYP exchange-correlation functional and 6-31G** basis set being used.

It is shown that molecules with hydroxyl groups are more stable as compared with fully coordinated ones.

A question arises about possibility of physical and chemical interactions between these molecules. This question was examined, the most little stable member of series of bubble silica molecules with hydroxyl groups $(SiO_2)_{20}(H_2O)_{10}$ being taken as an example. In this molecule silicon atoms are apical in twelve regular pentagons.

Two ways of intermolecular interaction of such molecules are considered.

According to the former, the calculation of intermolecular interaction energy for $(SiO_2)_{20}(H_2O)_{10}$ molecules caused by the formation of hydrogen bonds between hydroxyl groups was carried out. The calculations indicate that along with hydrogen bond, the Van der Waals forces make an essential contribution to this interaction.

The formation of a covalent bond between $(SiO_2)_{20}(H_2O)_{10}$ molecules is disadvantageous. This is connected with considerable repulsion forces arising between closely located terminal hydroxyl groups of generated dimmer.

Ascorbic acid stabilization on the silica surface: experimental and theoretical study

Olga Kazakova, Irina Laguta, Oksana Stavinskaya, Pavlo Kuzema

A.A. Chuiko Institute of Surface Chemistry of National Academy of Sciences, Gen. Naumov Street 17, 03164 Kyiv, Ukraine

E-mail: kazakova@voliacable.com

Oxidative stress or imbalance between formation and deactivation of free radicals is considered to be one of the main causes of many known human diseases. Being natural antioxidant of direct action the ascorbic acid (vitamin C) is the attractive object for prophylactic drug development. However, obtaining stable formulations remains a challenge since these vitamin are readily oxidized in a liquid medium. Immobilization of such biomolecules on solid surfaces may result in enhanced stabilization. Highly disperse silica is widely used in pharmaceutical formulations as a filler, adsorbent, thickener etc.

Adsorption of the ascorbic acid from aqueous and ethanol solutions on unmodified and partially hydrophobized nanosilica A-200 was studied using UV spectroscopy. Structural and electronic characteristics of model clusters of silica, their complexes with vitamins, and free energy of solvation (ΔG_s) have been calculated using the solvation model SM5.42 with the 6-31G(d) basis set (GAMESOL program package, Version 3.1). Antioxidant power of silica nanocomposites with immobilized ascorbic acid was evaluated by measuring the total polyphenolic index following the Folin-Ciocalteu method.

It has been shown that immobilization of ascorbic acid on silica surface leads to their stabilization. The rate of ascorbic acid oxidation to dehydroascorbic acid was found to be much less in the presence of unmodified or modified silica. On interaction of an ascorbic acid molecule with the surface of a silica particle in ethanol solution, the charges of hydrogen atoms of hydroxyls involved in the reaction of ascorbic acid oxidation are decreased. Thus, the decrease in proton-donor ability of OH groups of the adsorbate due to formation of hydrogen bonds with surface silanols probably leads to vitamin C stabilization in the presence of silica in ethanol. Similar processes take place on the surface of modified silica.

Being released from the carrier molecules of ascorbic acid do not lose their antioxidant properties.

Quantum chemical analysis of clusterization of substituted alkanes at air/water interface

Yu.B. Vysotsky,[a] E.A. Belyaeva,[a] D. Vollhardt [b]

[a]***Donetsk National Technical University, 58 Artema Str., 83000 Donetsk, Ukraine, yuvysot@cable.netlux.org***

[b]***Max Planck Institute of Colloids and Interfaces, D-14424 Potsdam/Golm, Germany***

Surface-active compounds are well known to have amphiphilic nature, i.e. they include polar and non-polar parts. Fatty *n*-alcohols, *n*-thioalcohols, *n*-carbon acides and *n*-amines were studied in this work. Their functional groups (OH-, SH-, -COOH and NH-) are polar, and the hydrocarbon radicals play role of non-polar parts. Molecules of surface-active compounds in water solution orient to the surface boundary: the polar group interacts with water, and the radical is popped on a surface. It was proved experimentally, that the surfactants are oriented to surface boundary with the angel about 81^0. The formation of films of surfactants at the air/water interface takes place with the some definite length of a hydrocarbon radical. In our opinion it could be explained by taking into account contributions from intermolecular hydrogen - hydrogen interactions of hydrocarbon radicals in the total energetic of clusterization. Only ab initio methods and semiempirical method PM3 take into account these interactions. Since using ab initio methods requires much machining time and the RAM, semiempirical method PM3 was used for calculations.

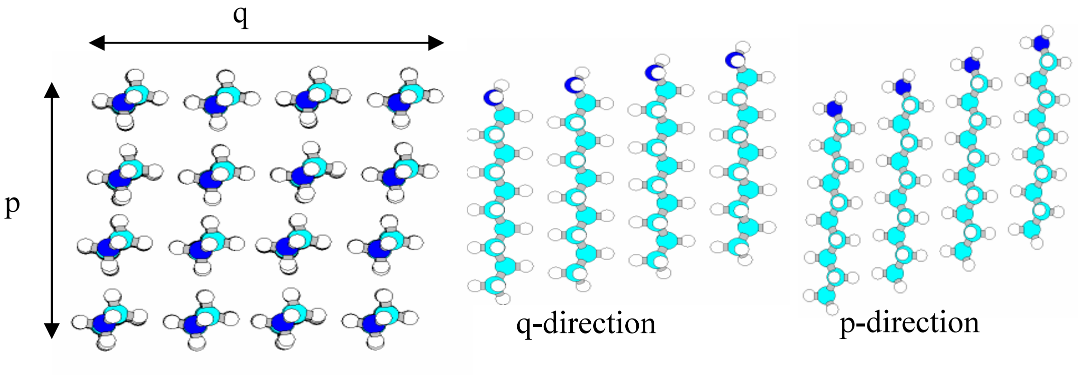


Fig.1

The thermodynamic parameters of clusterization of fatty *n*-alcohols, *n*-thioalcohols, *n*-carboxylic acids and *n*-amines with the length of a hydrocarbon radical from 6 up to 16 atoms of carbon were calculated (there were 302 compounds including corresponding monomers). First a conformation analysis of monomers was carried out by varying the torsion angle with the increment of 5. in the range 0^0 – 360^0.The dimers, trimers and tetramers of different structures were obtained from the corresponding monomers. The regression dependence of thermodynamic parameters (enthalpy, entropy and Gibbs energy of clusterization) on the number of interactions in functional groups and the number of carbon atoms in the chain, and also from a type of interactions was obtained. Received dependences for enthalpies and entropies of clusterization are steplike.

These dependencies provide calculations of thermodynamic parameters for clusterization of associates of any quantity, including infinite (see fig. 1, $q \to \infty$, $p \to \infty$). The spontaneous clusterization for alcohols is observed from 12 carbon atoms, for carboxylic acids and thioalcohols 14-15, for amines – from 18-20 atoms. Received results are in good agreement with the experimental data.

Molecular modeling study of polyene-sterol membrane channel

Yu.V. Lisnyak[a], A.V. Martynov[a], A.V. Gubskaya[b]

[a]*Molecular Modeling Laboratory, I.Mechnikov Institute of Microbiology and Immunology, Academy of Medical Sciences of Ukraine, Kharkov, 61057, Ukraine*

[b]*New Jersey Center for Biomaterials, Rutgers, The State University of New Jersey, NJ 08854, USA*

Polyene macrolide antibiotics, commonly represented by amphotericin B (Amph B) and nystatin (Nyst), are well known for several decades as membrane-acting agents that are widely used in medicine to treat advanced fungal infections. Polyene antibiotics (PA) exhibit a whole variety of valuable chemotherapeutical properties and despite of some side effects they are usually considered as major antifungal drugs due to their high efficacy [1]. It is of utmost importance to understand better molecular mechanisms of their biological functioning and to create solid grounds for structure-aided design of new PA derivatives with reduced side effects.

It has been shown that molecular mechanisms of PA functioning are closely related to their ability to form hydrophilic channels in hydrophobic environment of a cellular membrane that causes leakage of ions and other small molecules from a cell [2, 3]. Membrane sterols such as cholesterol and ergosterol also participate in formation of membrane channels as molecular targets for PA. Experimental molecular structure of polyene-sterol membrane channels (PSMC) has not been obtained yet and despite of the fact that PSMC were investigated in a number of experimental and theoretical studies [2,4] the structural specificity and characteristics of PSMC still remain subjects of discussion. In the absence of experimentally determined structural information on such channels, molecular modeling appears to be invaluable tool in studying a spatial organization of PSMC supramolecular aggregates, intermolecular interactions that involve their structural subunits and molecular mechanisms of antimicrobial function of membrane-acting agents. The present study of the structure of PSMC is supposed to bring new insights into this problem.

We present and characterize molecular models of PSMC designed for both single-length and double-length channels. Intermolecular interactions (including hydrogen bonding) between antibiotic and sterol molecules, which are involved in isolated dimer as well as in supramolecular PSMC complex, are analyzed. Structural features of our models such as dimensions and a shape of the channel and its pore, intermolecular hydrogen bonding pattern, participation of different functional groups in hydrophilic and hydrophobic intermolecular interactions are discussed and compared with those for PSMC models available from the literature. The proposed model structures of PSMC can be easily incorporated into phospholipid bilayer of a cell membrane to serve as an initial structure for further comprehensive molecular dynamics simulations of this system in the presence of aqueous environment.

[1] Hillery A.M. *Adv. Drug Deliv. Rev.* **24** (1997) 345.
[2] Baginski M., Czub J. and Sternal K. *Chem. Rec.* **6** (2007) 320.
[3] Kasumov Kh.M. The Molecular Basis of Polyene Antibiotics Functioning in Lipid Membranes – The Interplay Between Structure and Function. Doct. Thesis, Puschino (1979).
[4] Gagos M., Koper R. and Gruszecki W.I. *Biochim. Biophys. Acta* 1511 (2001) 90.

The quantum-chemical research of the chemisorptions in the catalytic processes

V.V. Kukueva

Fire Safety Institute, 18034, Onoprienko str. 8, Cherkassy, Ukraine

E-mail: kukueva@yahoo.com

In spite of the great amount of the theoretical and experimental research of chemical active spices, the interest to this field is increasing due to importance in the catalytic processes. 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. As well known adsorption is a process where molecules from the gas phase or from solution bind in a condensed layer on the solid or liquid surface. The nature of bonding between adsorbent and surface is still subject to some interpretation.

The quantum-chemical calculations have been provided by the *ab initio* method in the 6-31 basis set to investigate the chemical way to destruct of organic molecules immobilizing on the silica surface. Because the 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 phosphorus-containing radical ($PO^{\bullet}$, $NH_2^{\bullet}$, $PH_2^{\bullet}$) as one of the representatives of fire suppression agents [1]. 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	$E_{destr.\ bind.}$(kkal/mol)
$(OH)_3Si\text{-}PO \rightarrow (OH)_3Si^{\bullet} + PO^{\bullet}$	21,3
$(OH)_3Si\text{-} NH_2 \rightarrow (OH)_3Si^{\bullet} + NH_2^{\bullet}$	87,8
$(OH)_3Si\text{-}PH_2 \rightarrow (OH)_3Si^{\bullet} + PH_2^{\bullet}$	50,1

As we can see from the table, the more preferable destruction way from the silica surfaces is the abstraction phosphorus containing-radical. So the $PO^{\bullet}$ radical occur 2,4 times easy, than $PH_2^{\bullet}$, and 3,2 times less then from isolated molecule of ammonium phosphate. Consequently, it can be suggested that immobilization of $PO^{\bullet}$ radical on the silica surfaces can help to prolongation of inhibition action of this particle.

[1] Allen Twarowski, *Combustion and Flame* **105** (1996) 407-413.

Density Functional Theory Molecular Cluster Study of NO Chemisorption and Reactions on Metal Surface Cu(100)

I.I. Zaharov, A.V. Suvorin, A.I. Kolbasin, O.I. Zaharova

Volodymyr Dal East Ukrainian Natianal University, Severodonetsk Technological Institute, Severodonetsk 93400, Prosp. Radyanskyt, 59a, Ukraine

By quantum-chemical method of density functional theory DFT/B3LYP we have investigated of NO chemisorption and reactions on metal surface Cu(100). All calculations were carried out on the clusters Cu_{20} and Cu_{16}. The LANL2 effective core potential was employed for Cu atoms using the DZ basis set. The NO and $(NO)_2$ dimer were described using the 6-31G basis set.

The quantum-chemical researches have shown, that at adsorption NO on Cu only the molecular form was stabilized [1]. For the lack of an opportunity NO dissociation on Cu surface, the reaction mechanism with superficial N-O bond cleavage and formation of reduction products N_2 and N_2O till now remains unclear [2].

In the given work it is shown, that the reaction mechanism on a surface of copper includes a formation of the cis-dimer intermediate ($O_{(ad)}N\text{-}NO_{(ad)}$) with essentially strong N-N bond ($r_{N\text{-}N}$~1.23 Å). It is coordinated to a surface through O-atoms and manifests the high reactivity to dissociation of $N\text{-}O_{(ad)}$ (see fig. 1).

The very small calculated activation energy of a decomposition of the dimer intermediate ($O_{(ad)}N\text{-}NO_{(ad)}$) characterizes its kinetic instability and does not allow to identify its by modern experimental methods of the surface metal research. At the time for the MgO surface and in the individual complex $(Ph_3P)_2Pt(O_2N_2)$, the stable cis-dimer ($(O_{(ad)}N\text{-}NO_{(ad)}$) is experimentally identified.

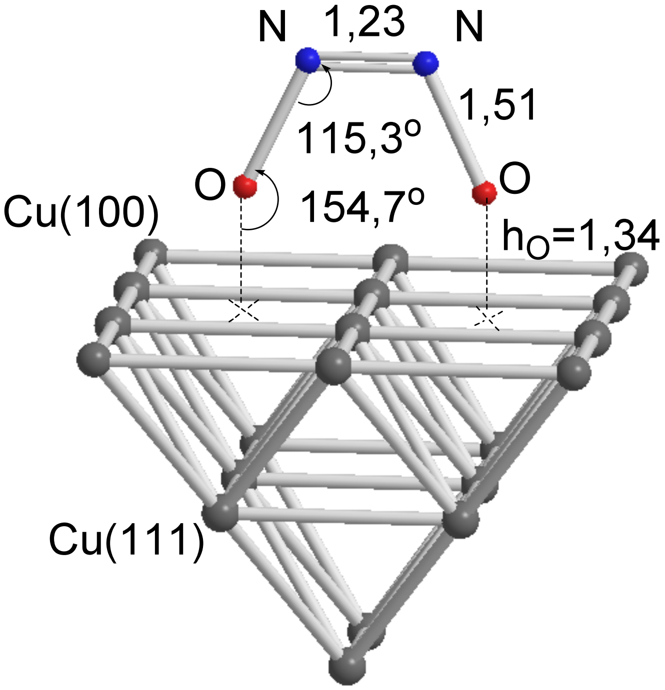


Fig. 1. The DFT calculated structure of dimer $O_{(ad)}N\text{-}NO_{(ad)}$ on the cluster Cu_{20}.

According to [3] it is shown, that the calculated reaction energy profile of cis-dimer ON-NO formation and decomposition on the copper surface characterizes the real low-temperature mechanism of NO reduction with small activation energy.

[1] Brown W.A., King D.A., *J. Phys. Chem.* B **104**(12) (2000) 2578.
[2] Haq S., Carew A., Raval R., *J. Catal.***221**(1) (2004) 204.
[3] Zakharov I.I., Ismagilov Z.R., Ruzankin S. Ph., Anufrienko V.F., Yashnik S.A., Zakharova O.I., *J. Phys. Chem.* C **111**(7) (2007) 3080–3089.

Contribution of the atomic structure of a surface to the interaction potential with the quantum size metal film in an external electric field

L.G. Il’chenko, T.V. Goraychuk and V.V. Lobanov

Institute of Surface Chemistry NAS of Ukraine, Generala Naumova Street 17, Kiev 03164, UKRAINE e-mail: Goraychuk @ukr.net

It is known that the characteristics of spatially - limited structures (quantum dots, quantum wells and superthin films), such as electron affinity, Fermi energy, work-function, etc., resulting from quantum-size (QS) effects differ critically from the same characteristics in the corresponding unlimited structures [1].

Meanwhile the pair charges interaction on the surface of the superthin films [2], the image potential [3], the structured potential [4] depending on the thickness d of the QS film and is a non-monotonic function of d. The non-monotonic dependence of the potential barrier on the thickness d of the QS film determines the thickness dependence of the QS metal films characteristics of the in an external electric field.

In this work, using of the nonlocal electrostatics methods [5], the influence of the microscopic (atomic) structure of the metal film surface on the ion-surface interaction potential depending on the electronic structure of metallic film and its thickness is determined. The complete interaction potential $V_N(\vec{r},F)$ of the charge e with the quasineutral surface of the QS film is calculated, when for $V_N(\vec{r},F)$ we have

$$V_N(\vec{r},F) = \Delta V_{st}^{N}(\vec{r}) + V_0^{N}(x) - eFx\,, \qquad (1)$$

where $V_0^N(x)$ is the image potential, which is determined by an electronic structure and the thickness d of the film [4], and $\Delta V_{st}^N(\vec{r})$ is the structured potential, which is determined by the microscopic (atomic) structure of the metallic QS film surface [5,6], F – is the electrical field. We shall limit discussion to the simplest long - wave Thomas-Fermi approximation (TFA) for the dielectric function $\varepsilon_N(\vec{k})$ of the QS film, because the TFA provides a correct account of the electronic structure of metals [1-3].

The full potential $V_N(\vec{r},F)$ in a vacuum region *x>0* of the thin metal film is calculated on the basis of the proposed model taking into account the size quantum of the electron energy spectrum and microscopic (atomic) structure of its surface. The full potential $V_N(\vec{r},F)$ has a quasi-oscillatory dependence on the QS film thickness. This non-monotonic dependence of $V_N(\vec{r},F)$ on the thickness d of the QS film can determine the dimensional dependence of the chemical processes (chemical adsorption, .dissociation) on (or near) the metallic QS film surface.

[1] L.G. Il’chenko, T.V. Goraychuk, *Ultramicroscopy* **95** (2003) 67-73

[2] L.G. Il’chenko, V.V.Lobanov, V.V. Il’chenko, *Physics and Chemistry of Solid State* **6**(4) (2005) 600-602.

[3] L.G.Il’chenko and T.V.Goraychuk, *Surface Sci.* **478** (2001) 169-179.

[4] L.G. Il’chenko, V.V.Lobanov // *Investigations on Sensor Systems and Technologies* // Edided by Anna V. El’skaya, Vitaliy D. Pokhodenko. Kyiv, pp .231-240 (2006).

[5] Il’chenko L.G. // *12th International Vacuum Microelectronics Conference* 6th-9th July 1999. Darmstadt, Germany, Technical Digest, pp.84-85 (1999).

The favorable mechanisms of interactions between benzoic acid and ethanol or methanol on a surface of vanadium dioxide

V.N. Kaurkovska

A.A. Chuiko Institute of Surface Chemistry of National Academy of Sciences, Gen. Naumov Street 17, 03164 Kyiv, Ukraine, e-mail: kavn@ukr.net

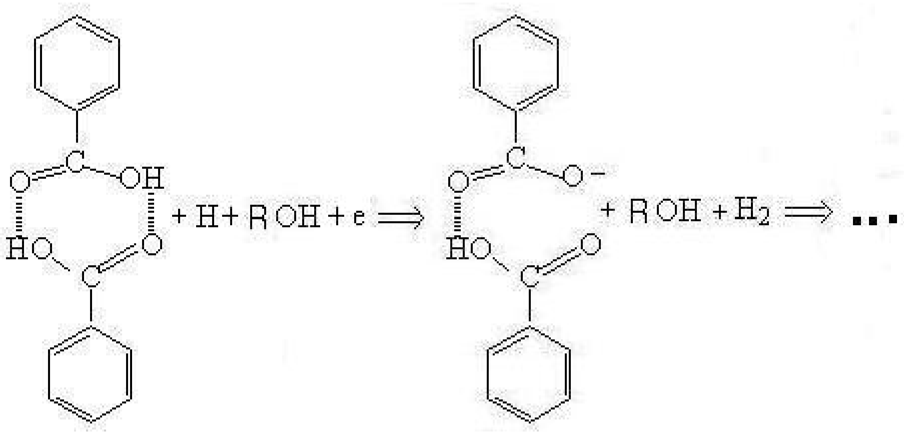
It is known that interactions of steams of ethanol or metanol with the benzoic acid inflicted from benzol solution on the surface of pill of VO_2 is accompanied the temporal decline of resistance. Intensity of splash of conductivity is increased at growth of temperature, and also after the preliminary irradiation of surface of pill of gamma-quants [1].

Quantum chemical analysis of interactions on the surface of oxide with the phase transition of semiconductor–metal (T_c=338-340k) is based on suppositions: 1) in area of temperatures of coexistence of two phases (T_c±30k) connection of easy molecules with a surface is weak; 2) in co-operations of reagents do the electrons of conductivity and mobile products of dissociation or radiation-chemical transformations of molecules of water take part on the surface of hard oxide: protons, atoms of hydrogen, hidrid-ions.

Criteria of choice of model: lowering of complete total energy, small values of energy of excitation of the system, thermodynamics permitted a reaction (co-operations), high affinity to the electron.

Modeling of interactions was carried out by means of the PC GAMESS 6.0 program.

Advantageous chart:



Dissociation of H-H on metals is known. The transfer of charge on a chart proceeds to formation of a layer with smaller conductivity on a surface (joining OH). Such model can explain the successive lowerings and increases of resistance a surface at the mentioned interactions.

[1] V. N. Kaurkovskaya, L. S. Dzyubenko, A. P. Shakhov, V. N. Doroshenko, and A. A. Chuiko // *High Energy Chemistry* **4** (2006) 212.

DFT modeling of structural parameters of Si(111) doped with hydrogen atoms

A.M. Saad[a], A. L. Pushkarchuk[b], V. A. Pushkarchuk[c], A.V. Mazanik[d],
O.V. Zinchuk[d], A.K. Fedotov[d]

[a]Al-Balqa Applied University, P.O. Box 204,1Amman 11953, Jordan

[b]Institute of Physical – Organic Chemistry NASB, Surganova, 13 220072 Minsk, Belarus, alexp51@bk.ru

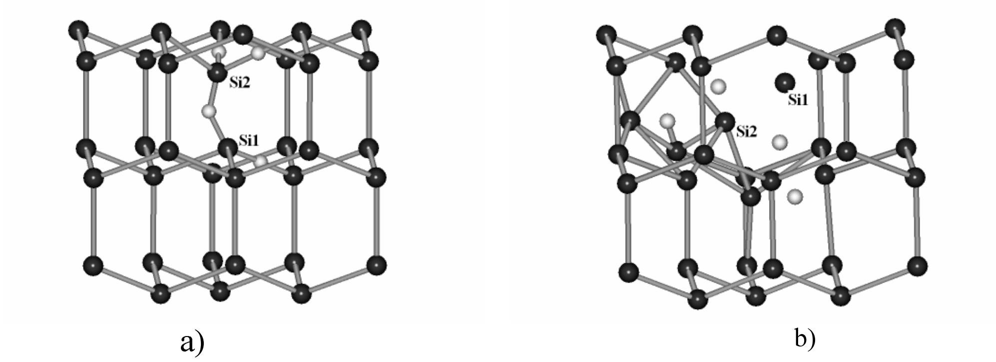
[c]Belarusian State University of Informatics and Radioelectronics, P. Brovka 6, 220013 Minsk, Belarus

[d]Belarusian State University, Independence av. 4, 220050 Minsk, Belarus

At the present time we are realizing an intense experimental study of near surface silicon layer reconstruction due to low energy ion-beam hydrogen treatment. As is shown experimentally, at the surface of Si wafer hydrogenated at 300 K an oxygen-containing dielectric layer is formed [1]. The properties of this layer differ from the silicon oxide ones. For the understanding of reasons and mechanisms of arising dielectric layer, quantum-chemical analysis of the influence of H atoms, introduced into Si lattice, on the atomic structure of near surface Si layers is of great importance.

Here we present the results of systematic theoretical studies of atomic configurations and electronic properties of various silicon clusters with incorporated interstitial H atoms ([H]), obtained by semiempirical (PM3) and DFT quantum-chemical methods. The hydrogen-passivated silicon clusters $Si_{35}H_{30}[H_N]$ and $Si_{71}H_{74}[H_N]$ (N=1-4 number of H impurity atoms in cluster) were considered for modeling of (111) Si surface containing H-containing complexes. The PM3 and DFT geometry optimization procedure were used to various H-containing impurity complexes in clusters, other part of clusters were fixed.

The example of calculated atomic configurations of $Si_{35}H_{30}[H_4]$ cluster before and after geometry optimization procedure is presented in Fig. 1.



a) b)

Figure 1. The atomic configurations of $Si_{35}H_{30}[H_4]$ cluster a) before geometry optimization procedure and b) after geometry optimization procedure. Black balls represent Si atoms. Si1 – central atom of unrelaxed cluster, Si2 – second surface atom of unrelaxed cluster.

The obtained results show that incorporation of H-atoms into Si results in very strong disturbance of the near-surface region of Si lattice.

The software package PC GAMESS [2] based on GAMESS (US) [3] was used. The DFTcalculations were performed with the B3LYP1 functional and MINI basis.

[1] O. Zinchuk, N. Drozdov, A. Mazanik, A. Fedotov, P. Zukowski, J. Partyka, P. Wegierek, T. Koltunowicz, *Vacuum* 2007 (in press).

[2] Granovsky Alex., www http://classic.chem.msu.su/gran/gamess/index.html

[3] Schmidt M.W. et. al., *J.Comput.Chem*. **14** (1993) 1347.

Intermolecular interactions and stability of the nanoparticles of inorganic compounds with chain structure: quantum chemical study

A.G. Grebenyuk

A.A. Chuiko Institute of Surface Chemistry of National Academy of Sciences, Gen. Naumov Street 17, 03164 Kyiv, Ukraine, e-mail: grebenyuk_ag@ukr.net

The modern solid state chemistry considers the search for relations between the structure and properties of various compounds as its main task. In case of nanoparticles, a problem arises on the role of surface layer in their equilibrium spatial structure and reactivity. The application of quantum chemical methods to the design of structural models for crystals and nanoparticles makes the results obtained more informative. One-dimensional (chain) structures can be easily examined theoretically within either periodical or cluster approximations. Use of the cluster approach assumes isolation of a definite part of crystalline lattice, and frontier conditions should be satisfied for edge atoms. Since the most of inorganic compounds is characterized by a hypervalent structure where coordination numbers of the atoms or ions exceed their normal valences, examining their cluster models is of particular interest.

When classified, hypervalent chain structures can be divided into some groups depending on the coordination number of structure-forming atoms as well as on the quantity of monoatomic bridges connecting these atoms. For example, AuI forms simple chains where atoms of both types are two-coordinated and I-Au-I fragments are linear. Beryllium dihalogenides (except BeF_2) is formed by distorted beryllium-halogen tetrahedrons with shared edges (similar to w-silica). Unlike those, $PdCl_2$ is characterized by planar $PdCl_4$ squares. Rutile TiO_2 is believed to be a formally chain structure due to a definite deviation between axial and planar Ti-O bonds. The structure of ZrI_3 chain has sixfold coordinated zirconium atoms surrounded by six two-coordinated iodine atoms divided into two triple bridges. Finally, uranium (IV) acetylacetonate chain has cubic coordination of metal atoms connected by two fourfold ligand bridges. Another peculiarity of such structural class can be the presence of additional atoms attached to the main chain, for example, those in $SnCl_2$, TeF_4, or $CdCl_2*2NH_3$.

Due to the lack of atoms required to complete the coordination sphere of the edge atoms (what is a characteristic of any hypervalent structure) of the clusters, sometimes their equilibrium statial structure can be distorted or even rearranged under geometry optimization resulted in the saturation of coordination valences. The formation of intermolecular complexes with additional small molecules or by some oligomeric chains stationed in parallel can help to avoid such an unwanted side effect. Besides, in case of rigid chain, no cyclic structures can be achived advantageous in energy as compared with chain one.

Quantum-chemical investigations of TICT-process in some molecules containing aminogroups

T.V. Sakhno, T.P. Romashko, O.A. Khakhel'

Poltava Department of Ukrainian Academy of Technological Cybernetics Sciences, Poltava, Ukraine

TICT-process (Twisted Intramolecular Charge Transfer) is the photophysical phenomenon, which is taking place for a class of molecules with a certain structure. The given structure assumes presence in molecules of amino groups with the alkyl substituents capable to a twisting relaxation around the C(Ar)-N(amino) bond. This relaxation occurs in molecules after electronic excitation. Thus, the equilibrium structures of the ground and excited states of these molecules are different. Twist-conformation of amino groups in an excited state is favorable for intramolecular charge transfer, where the amino group acts as the donor in the TICT-state.

TICT-process has been found out spectrally. Together with normal fluorescence of molecules, the red-shifted TICT-band is observed in their spectra of fluorescence. Its manifestations are substantially defined by media polarity, the nature of a matrix (liquid solution, rigid environment), etc.

An opportunity of proceeding of the TICT-process in those or other molecules is proved, mainly, by quantum-chemical calculations. Their results lead at times to inconsistent conclusions concerning formation of the TICT-state in molecules. In the literature there is a number of examples, where the calculations of different authors carried out by various methods give opposite forecasts for efficiency of TICT.

In the present work, the comparative analysis of data of quantum-chemical calculations conducted by semi empirical methods and within the frame of ab initio approaches (package Gaussian 03) for some molecules (Nile Red, 7-amino-coumarin derivatives, (dimethylamino) stilbazolium dyes, naphthalene aminoderivatives and some others) is carried out. The obtained results are discussed in a context of results of spectral experiments.

Charge and geometrical solitons in unsymmetrical cyanine dyes

O.B. Ryabitsky, O.D. Kachkovsky

Institute of Organic Chemistry, National Academy of Sciences, Murmanskaya 5, Kiev, 03094, Ukraine

Cyanines as a special type of cationic polymethine dyes are well-known because of their unique ability to conversion of the light energy. The main chromophore/flourophore consists of the extended polymethine chain restricted by two tree-coordinated nitrogen atoms. The total positive charge was found to be not delocalized uniformly along the whole chromophore, but it generates a solitonic-like wave of the alternated partial positive and negative charges [1]. It was shown that this wave (soliton or polaron) in the unsubstituted polymethine cations **1** is of finite dimension, approximately 15-17 carbon atoms.

$$H_2C^+ - (CH = CH)_n - CH = CH_2 \qquad \mathbf{1}$$

Since the polymethine chain is a non-rigid π-electron system, then the wave of the partial charges causes the corresponding rearrangement of the molecular geometry, primarily, the carbon-carbon bond length. According to quantum-chemical calculation, the lengths of the equilibrium CC-bonds are practically equaiized in the chain segment where the soliton is located. Introducing of the terminal groups leads to considerable change of the shape and location of the solitonic wave; so, in the dimethylamino-polymethines (streptocyanines), the centre of the soliton could be shifted to one of the end groups, if the length of the chromophore exceeds the charge wave dimension; i.e., the symmetry breaking of the electron density distribution and molecular geometry occurs [1,2]. Meanwhile, symmetry of electron structure in the neutral polyenes with the same terminal residues (dimethyl-aminogroups) remains even in the molecules with the comparative long polymethine chain.

In the same time, the going from symmetrical dyes to unsymmetrical cyanines influences significantly on the electron distribution and hence on spectral properties. It was found that the position of the maximum for an unsymmetrical dyes λ_{as} is shifted towards short wavelengths as compared to the arithmetic mean value from the maxima of the parent dyes. This spectral fact was treated to be connected with an appearance of the alternation of the CC-bond length along the polymethine chain, if terminal groups are non-equivalent. One could expect that unsymmetrical chemical constitution should cause shifting of the charge and geometrical solitons from the chain centre. It turn, this shifting should depends on the difference in donor strengths of the both terminal groups.

The results of the quantum-chemical study of the shape and location of solitons in the unsymmetrical cyanine dyes are presented by this work. As unsymmetrical polymethines, the mono-substituted dyes **2** and dyes with different terminal groups R_1 and R_2 **3** were considered.

$$H_2C^+ - (CH = CH)_n - CH = CH - R \quad \mathbf{2} \qquad\qquad R_1^+ = CH - (CH = CH)_n - R_2 \quad \mathbf{3}$$

Here R, R_1, R_2 can be both donor and acceptor substituents conjugated with the main polymethine chain: OCH_3, SCH_3, $N(CH_3)_2$, CH=O, NO_2, as well as the simplest heterocyclic residues.

[1] A.D.Kachkovsky, The solitonic nature of the electronic structure of the ions of linear conjugated systems. *Theoretic and Experimental Chemistry* **41** (2005) 139-164.

[2] A.B.Ryabitsky, A.D.Kachkovsky, O.V.Przonska, Symmetry breaking in cationic and anionic polymethine dyes. *J.Molec Struct. (THEOCHEM)* **802** (2007) 75-83.

Comparison of various perturbation theory quantum-chemical methods on example of XYCO (X,Y=H,F,Cl) molecules in lowest excited electronic states

S.I. Bokarev, V.A. Bataev, I.A. Godunov

Chemistry Department, Moscow State University, 119992 Moscow Russia, E-mail: bokarev@phys.chem.msu.ru

It was proved experimentally for the wide variety of aliphatic carbonyls that upon electronic excitation from ground (S_0) to the lowest excited singlet (S_1) or triplet (T_1) states carbonyl fragment becomes pyramidally distorted and there appear large-amplitude vibration (inversion) which may significantly influence the photophysical and photochemical molecular properties. But experimental data are not sufficient to completely understand the structure of carbonyls in excited electronic states and important information can be obtained by carrying out the reliable quantum-chemical calculations. Besides accuracy theoretical methods are to be computationally efficient to study large areas of the PES of a non-rigid systems.

We have used a large number of single-reference (SR) and multi-reference (MR) methods and SR and MR perturbation theory (PT) methods appeared to be the most effective to study even large areas of a PES. As several approaches to do PT calculations exist we aimed to compare them. For this purpose UMP2, MR-MP2, CASPT2, CASPT3, and NEVPT2 methods were chosen. The following molecular parameters were the point of investigation: geometries of stationary points, barriers to inversion, and adiabatic $T_1 \leftarrow S_0$ and $S_1 \leftarrow S_0$ transition energies of the simplest representatives of carbonyls XYCO (X,Y=H,F,Cl).

According to our results all PT approaches are rather similar. As other SR and MR methods PT approaches significantly overestimate barrier to inversion for F_2CO molecule but for other species they in general demonstrate agreement with experimental data. CASPT2 method is the most appropriate to study carbonyl molecules in excited electronic states because of its accuracy and efficiency. Results obtained by all methods are only slightly dependent on basis set but strongly on the active space used.

This work was financially supported by the Russian Foundation for Basic Research (grant N 07-03-00090).

Structure and conformational dynamics of acrolein molecule in the ground and lowest $^{1,3}(n,\pi^*)$ excited electronic states

O.S. Bokareva, V.A. Bataev, V.I. Pupyshev, I.A. Godunov

Chemistry Department, Moscow State University, 119992 Moscow Russia, E-mail: bokarevaos@phys.chem.msu.ru

Potential energy surface (PES) sections of acrolein molecule (CH_2=CH−CHO) in the ground and $^{1,3}(n,\pi^*)$ excited electronic states are studied to understand the peculiarities of internal rotation of carbonyl containing molecules. The following quantum chemical methods were used MP2, B3LYP, QCISD, CCSD(T) (for S_0 state); UMP2, PBE0 (for $^3(n,\pi^*)$), CASSCF, MR-MP2 (for $^{1,3}(n,\pi^*)$ states) with AO basis sets of the level 6-311++G(d,p) and cc-pVTZ.

The geometrical parameters of stationary points and vibrational motions of nuclei are studied. Different types of one-dimensional sections of PES, such as section along torsion coordinate, minimal energy path (MEP) and intrinsic reaction coordinate (IRC) are considered. The estimations of corresponding torsion frequencies are obtained from these sections. Values of energy differences between *s-cis* and *s-trans* conformers (S_0, $^3(n,\pi^*)$) and barrier to internal rotation (S_0) were determined more precisely using Valence Focal-Point Analysis technique [see e.g. A.G. Császár, W.D. Allen, H.F. Shaefer III, *J. Chem. Phys.* **108** (1998) 9751].

For $^{1,3}(n,\pi^*)$ excited electronic states some unusual features of internal rotation were found being not known for the ground state. For example, one-dimensional torsion MEP corresponding to the rotation relative to the ordinary C-C bond has significant curvature: internal rotation is accompanied by significant (more than 30°) non-planar distortion of carbonyl fragment. Such character of PES shows strong coupling of torsion and out-of-plane C−H bending motions. It is also important, that MEP has bifurcation points and in certain areas corresponding to torsion angle near 90° there exists an ambiguity in building MEP.

The two-dimensional approach was used for the analysis of torsion vibrations. In particular, this approach provides information about coupling of torsion and out-of-plane C-H bending vibrations. The results obtained are in a good agreement with experimental data.

This work was financially supported by the Russian Foundation for Basis Research (grants NN 07-03-00090, 07-03-01021).

Theoretical Investigation of Structute and Conformational Dynamics of the Cyclopropanecarboxaldehyde Molecule in the Ground and Excited Electronic States

E.V. Rastoltseva, V.A. Bataev, I.A. Godunov

Department of Chemistry, M.V. Lomonosov Moscow State University, 119992 Moscow Russia, E-mail: rastoltseva@phys.chem.msu.ru

The peculiarities of structure and vibronic spectra of the cyclopropanecarboxaldehyde (CPCA) obtained from *ab initio* calculations are discussed.

Systematic *ab initio* calculations of CPCA molecule for the ground electronic state were performed using various approaches, including B3LYP, CCSD and CCSD[T] methods and various Pople and Dunning basis sets. In these approaches the equilibrium geometry, harmonic and unharmonic frequencies, conformer energy difference, value of the barrier to internal rotation were calculated for the CPCA molecule. It turned out that in the ground state CPCA has two conformers: cis- and trans- with energy difference near zero (according to experiment energy difference is 60 cm^{-1}, cis-conformer is more stable). In order to obtain more precise result VFPA analysis of the conformer energy difference was performed.

And also torsion one-dimensional sections of the potential energy surface were evaluated and using them the anharmonic torsional energy levels were calculated variationally. The results obtained are in good correspondence with the experimental data.

CPCA demonstrate conformational changes upon electronic excitation. The $n \rightarrow \pi^*$ transitions to the lowest singlet and triplet electronic states lead to the rotation of the carbonyl group relatively the cyclopropane ring besides this the carbonyl fragment became non-planar. As a result there are six minimums on the potential energy surface which correspond to three pairs of enantiomers. Using UHF, MP2 and CASSCF methods with 6-31G* and cc-pVTZ basis sets equilibrium geometries, harmonic and anharmonic frequencies and barriers to internal rotation and inversion of non-planar carbonyl fragment were obtained. In addition, various one- and two - dimensional sections of the potential energy surfaces were evaluated and using them the anharmonic torsional, inversional and torsional-inversional energy levels were calculated variationally. The results obtained in this work provide new data for reinterpretation of vibronic spectra of CPCA obtained earlier [1].

This work is financially supported by the Russian Foundation for Basic Research, grant № 07-03-00090.

[1] Godunov I. A. et. al., *Russ. J. Phys. Chem.* **66** (1992) 515-519, 519-521.

Calculated spectral properties of Perylene Orange, Perylene Red and their complex with sodium azide

I. S. Irgibaeva[a], A. A. Aldongarov[a], N. N. Barashkov[b]

[a]***L. N. Gumilyov Eurasian National University, Astana, Kazakhstan, e-mail: irgsm@mail.ru***
[b]***Micro Tracers, Inc, San Francisco, CA***

Using the method of density functional theory in approximating B3LYP with the basis set 6-31G(d) the computations of structures of the following dyes 2,2'-N,N'-di(1,3-diisopropylbenzene)-diimide 3,4,9,10-perylenetethracarbon acid (Perylene Orange - PO) and 1,6,7,12-tethraphenyl ether 2,2'-N,N'-di(1,3-diisopropylbenzene)-diimide 3,4,9,10-perylenetethracarbon acid (Perylene Red - PR) were performed. It was revealed that PO and PR have nonplanar structures. On the basis of the predicted geometrical structures and molecular orbitals of S_0 ground state their theoretical UV-vis spectra, which are in good agreement with experiment, were obtained by applying time-dependent DFT (TDDFT) method. In addition, the calculations of complex [PR…NaN_3] and its UV-vis spectrum, which was compared with the observed electron spectrum of PR ethanol solution in the presence of NaN_3 under the laser irradiation at 532 nm, were carried out. By using DFT method at B3LYP level the calculations of the assumed complex were made where the reaction coordinate was the distance between Na^+ and carbonyl group O atom. It was suggested that [PR…NaN_3] complex formation involves transition of PR to the triplet state which brings about formation of PR anion. New peak at 793 nm in UV-vis spectrum of this solution under the laser irradiation at 532 nm is supposed to be a PR anion band.

Shape and location of charge and geometrical solitons in α.ω-disubstituted polyene dications

D.O. Melnik[a], O.D. Kachkovsky[b]

[a]Ivano-Frankivsk National Technical University of Oil and Gas, Karpatska 15, Ivano-Frankivsk, 76019, Ukraine

[b]Institute of Organic Chemistry, National Academy of Sciences, Murmanskaya 5, Kiev, 03094, Ukraine

Linear conjugated compound are excellently important for numerous applications in materials because their ability to absorb and emit the light in the visible and near IR spectral region; they exhibit highly intensive and comparatively narrow absorption and fluorescence band. This unique spectral property is found to be due to specific electron distribution in the chromophore and equilibrium molecular geometry in the ground and excited states of the neutral molecules and their ionic derivatives. According to present view, the injection of the electron or hole in the highly-polarized collective system of π-electrons causes the appearance of the so-called solitonic level (impurity level) in the energy gap and the considerable shift of the both conductive band bottom and valence band top [1,2]. The injected charge (electron or hole) is not delocalized uniformly over whole π-system, but is self-localized in the form of the solitary wave, i.e. a kink or soliton. The quantum-chemical calculations have shown that the charge wave is of a finite: approximately, 15-17 carbon atoms. When the chromophore length exceeds the dimension of the soliton wave, the soliton becomes mobile, in so far as it can be positioned in any fragment of the conjugated chain whithout change in the total energy of molecule.

Simultaneously with the charge wave, there apperars a geometrical or topological soliton, i.e. a solitonic-lake wave of the alternated of bond lengths, the shape and location of the bond length wave and charge wave being mutually connected.

The injection of multiple charges should necessarily generate the corresponding number of the solitons. Similar situation is realized, for example, in the charged derivatives of the polyenes or their α,ω-disubstituted analogs. However, their dimensions and locations are not studied as detailed as solitons in the monocations or monoanions. This work presents the results of the systematical investigation of the dimensions and locations of the geometrical and charge solitonic waves in the uncharged of the α.ω-disubstituted polyenes: $R–(CH=CH)_n–R$; and the dications of the α.ω-disubstituted polyenes containing the simplest donor terminal groups, $R^+–(CH=CH)_n–R^+$.

Where: $R = –CH=CH_2$; $–OH$; $–SH$ and $–N(CH_3)_2$.

[1] A.D.Kachkovsky, The solitonic nature of the electronic structure of the ions of linear conjugated systems. *Theoretic and Experimental Chemistry* **41** (2005) 139-164.

[2] A.B.Ryabitsky, A.D.Kachkovsky, O.V.Przonska, Symmetry breaking in cationic and anionic polymethine dyes. *J.Molec Struct.* (THEOCHEM) **802** (2007) 75-83.

Aldongarov A.A. 102
Alexandrova D.I. 77
Anglada J.M. 20
Antipin M.Yu. 9, 80
Antonovich V.P. 77
Artemenko A.G. 30, 76, 77, 78, 106
Assfeld X. 8, 57, 62
Babyuk D. 25
Barashkov N.N. 102
Bas D. 57
Bataev V.A. 38, 99, 100, 101
Belkina O.S. 24
Belous L.F. 61
Belyaeva E.A. 89
Bickelhaupt F.M. 19
Bokarev S.I. 38, 99
Bokareva O.S. 38, 100
Boldeskul I. 70
Bolshakov V.I. 40
Bondarover D.V. 30
Borisenko V.E. 82
Burda J.V. 17, 35
Chalmet S. 20
Chass G. 34
Cheranovskii V.O. 27
Chobal O.I. 84
Chotii C.Yu. 49
Desenko S.M. 48
Dmitruk A.F. 49, 51
Drobit'ko I.K. 73
Dyguda-Kazimierowicz E. 14
Dyshlovoj V.I. 54
Ezerskaya E.V. 27
Farafonova A.V. 52
Fedotov A.K. 95
Fedyanin I.V. 80
Fesenko S.I. 39
Filonov A.B. 82
Früchtl H.A. 53
Futera Z. 17
Galat V.F. 43
Gaponov A.A. 50
Glushkov V.N. 24, 39, 42
Godunov I.A. 38, 99, 100, 101
Golius A.M. 65
Golovenko N.Ya. 30
Goraychuk T.V. 93
Gorb L. 15, 58, 64, 72
Grebenyuk A.G. 96
Gromov L. 28
Gryn'ova G.V. 56
Gubskaya A.V. 90
Gutiérrez-Oliva S. 35
Hoggan P.E. 5
Hordienko O.V. 81
Hovorun D.M. 59, 63
Hushcha T.O. 37, 71
Il'chenko L.G. 93
Ilkevych N.S. 49
Irgibaeva I.S. 102
Isaev E.A. 56
Ivanov V.V. 41
Kachkovsky O.D. 98, 103
Kalchenko V.I. 79
Kaplan I.G. 3
Karachevtsev M.V. 68
Karachevtsev V.A. 68
Karwowski J. 6
Kasyan L.I. 50, 56
Kaurkovska V.N. 94
Kazakova O. 88
Khakhel' O.A. 97
Khavryuchenko O. 32, 36
Khavryuchenko V. 32, 36, 70, 86
Kholod Ya. 58
Khromov A.I. 76
Kilin S.Ya. 82, 83
Klimenko T.A. 41
Kochina O.S. 63
Kolbasin A.I. 54, 92
Konovalova I.S. 81
Kornilov M.Yu. 81
Korotkova I.V. 73
Kouts V. 28
Krasovska M.V. 67
Kravchenko I.V. 54
Kryachko E.S. 29
Kukueva V.V. 91
Kuten S.A. 82, 83
Kuvaeva Z.I. 75
Kuzema P. 88
Kuz'min V.E. 30, 76, 77, 78, 106
Laguta I. 88
Latajka Z. 18
Leontiev V.S. 68
Leszczynski J. 13, 15, 40, 50, 55, 58, 60, 64, 72
Liahovskiy A.V. 78, 106
Lisnyak V.V. 36
Lisnyak Yu.V. 90
Lobanov V.V. 69, 87, 93
Loos P.-F. 62
Luzanov A.V. 26
Lyakh D.I. 41
Lyssenko K.A. 9, 80
Lytvyn O.S. 68
Mach P. 12
Maga I.M. 74
Mamedov T.N. 83
Mansergas A. 20
Manthe U. 31

Martins-Costa M.T.C. 20
Martynov A.V. 90
Mazanik A.V. 95
Melnik D.O. 103
Miroshnychenko K.V. 47, 65, 66
Mokdad A. 60
Mons M. 10
van Mourik T. 11, 53
Muratov E.N. 30, 106
Murray J.S. 35
Nizovtsev A.P. 82, 83
Ognichenko L.N. 77, 106
Okovytyy S.I. 40, 50, 55, 56, 58, 72
Omelchenko I.V. 45
Opeida I.A. 51
Ostapenko N. 86
Palamarchuk G.V. 64
Papp P. 12
Petrova N.V. 33
Petrova T. 72
Pickard C.J. 53
Plakhotnyk V. 55
Poater J. 19
Polischuk O.V. 87
Polishchuk P.G. 76
Politzer P. 4, 35
Pomeshchenko A.I. 51
Prezhdo O. 22
Pupyshev V.I. 100
Pushkarchuk A.L. 75, 82, 83, 95
Pushkarchuk V.A. 82, 83, 95
Rastoltseva E.V. 38, 101
Réblová K. 60, 67
Rhodes M.M. 67
Rizak I.M. 84
Rizak V.M. 84
Romashko T.P. 97
Rossikhin V.V. 40, 55
Roszak S. 23
Rozhenko A.B. 31
Rubin Yu.V. 61
Ruiz-López M.F. 20
Ryabitsky O.B. 98
Rybachenko V.I. 49
Saad A.M. 95
Sakhno T.V. 73, 96
Sakhno Yu.E. 73
Samijlenko S.P. 59
Sefcikova J. 67
Semanin A.V. 44
Shchechkin I.E. 37, 71
Shestopalova A.V. 47, 65, 66
Shishkin O.V. 15, 45, 46, 48, 64, 79, 81
Shishkina S.V. 48, 79, 81
Shivanyuk A.V. 79
Shoeller W.W. 31
Sokalski W.A. 14
Solà M. 19
Soldatov V.S. 75
Solkan V. 85
Špačková N. 67
Šponer Jiří 16, 60, 67
Šponer Judit 60
Staemmler V. 12
Stavinskaya O. 88
Stepanian S.G. 68
Stepanyugin A.V. 59
Strelko V. 32
Sukhanov O.S. 47
Sukhodub L. 70
Suvorin A.V. 92
Svjatenko L.K. 50
Sychrovský V. 60
Tarabara I.N. 50, 72
Tarasenko Yu. 32
Tiurina T.G. 52
Tokar A.V. 56
Toro-Labbé A. 35
Tsendra O.M. 69
Tunega D. 21
Urban J. 12
Vollhardt D. 89
Voronkov E.O. 40
Vysotsky Yu.B. 89
Walter N.G. 67
Wielgus P. 23
Wilson S. 24
Woollins J.D. 53
Wyatt R.E. 25
Yakovkin I.N. 33
Yakuba A.A. 61
Yaryshkina L. 55
Yegorova A.V. 77
Yevtushenko O. 28
Yurenko Y.P. 59
Zaharov I.I. 54, 92
Zaharova O.I. 54, 92
Zaitseva V.V. 52
Zarechnaya O.M. 49, 51
Zhikol O.A. 26
Zilberberg I. 7
Zinchuk O.V. 95
Zubatyuk R.I. 45, 46, 81

The comparative analysis of efficacy of hierarchical informational technology for quantitative structure-activity relationships (HIT QSAR)

V.E. Kuz'min[a], A.G. Artemenko[a], E.N. Muratov[a,b], L.N. Ognichenko[a],
A.V. Liahovskiy[a]

[a]A.V.Bogatsky Physico-Chemical Institute of the National Academy of Sciences of Ukraine, 86 Lustdorfskaya doroga, Odessa 65080, Ukraine; E-mail: victor@2good.org

[b]Computational Center for Molecular Structure and Interactions, Jackson State University, Jackson, Mississippi, USA

The purpose of this work is the comparison of hierarchical informational technology (HIT) on the base of simplex representation of molecular structure (SiRMS)[1,2] with the most popular present-day QSAR approaches. The HIT QSAR is destined for optimization of new effective antivirals creation process. Due to the hierarchic strategy on each stage of this technology QSAR task is not solved *ab ovo*, but with the use of information received from a previous stage. In fact, it is proposed to deal with the system of permanently improved solutions, based on 1D - 4D molecular models. The SiRMS has been used in the developed technology. In the frames of SiRMS any molecule can be represented as the system of different simplexes (tetratomic fragments of fixed composition, structure, chirality and symmetry). Such representation allows unifying description of spatial structure of compounds with saving of complete stereochemical information. It enables to define molecular fragments increasing or decreasing biological activity of investigated compounds.

A set of 114 angiotensin converting enzyme (ACE) inhibitors and 111 acetylcholinesterase (AchE) inhibitors has been taken from the work [3]. It is necessary to note that all of explored compounds are structurally homogeneous, that facilitates the procedure of molecules superposition in lattice methods. We have compare in the given work the resulting PLS-models [3] built with the use of descriptors generated in the followings QSAR approaches:

a) CoMFA – Comparative Molecular Fields Analysis;
b) CoMSIA – Comparative Molecular Similarity Indexes Analysis;
c) EVA – Eigenvalue Analysis;
d) HQSAR – Hologram QSAR;
e) Cerius 2 program package – method of traditional integral (whole-molecule) 2D и 2.5D[3] descriptors generation;
f) HIT QSAR.

The advantages HIT QSAR method over others has been revealed by the comparison of such statistical descriptions of QSAR models, as determination coefficient for training (R^2) and test (R^2_{test}) sets; determination coefficient, calculated in the cross-validation terms (Q^2); as well as the standard errors of prediction for both sets. For example i) for the set of ACE inhibitors HIT QSAR Q^2= 0.82-0.89, R^2_{test}= 0.72-0.85, and for the other methods Q^2 = 0.66-0.72, R^2_{test}= 0.30-0.52 ii) for the set of AchE inhibitors HIT QSAR Q^2= 0.70-0.78, R^2_{test}= 0.74-0.77, and for the other methods Q^2 = 0.32-0.52, R^2_{test}= 0.16-0.47. Moreover, SiRMS based QSAR models allowing determining structural fragments with positive or negative influence on investigated property, as well as the contribution of different physical-chemical factors in the activity changes.

V.E.Kuz'min, A.G.Artemenko, R.N.Lozitska, A.S.Fedtchouk, V.P.Lozitsky, E.N.Muratov, A.K.Mescheriakov, *SAR and QSAR in Env. Res*. **16**(3) (2005) 219-230.

V.E. Kuz'min, A.G. Artemenko, P.G. Polischuk, E.N. Muratov, A.I. Khromov, A.V.Liahovskiy, S.A. Andronati, S.Yu. Makan, *J. Mol. Mod.* **11** (2005) 457-467.

J. J. Sutherland, L. A. O'Brien, D.F. Weaver, *J. Med. Chem.* **47** (2004) 5541-5554.

---

[3] This classification is offered by the authors of Cerius 2.