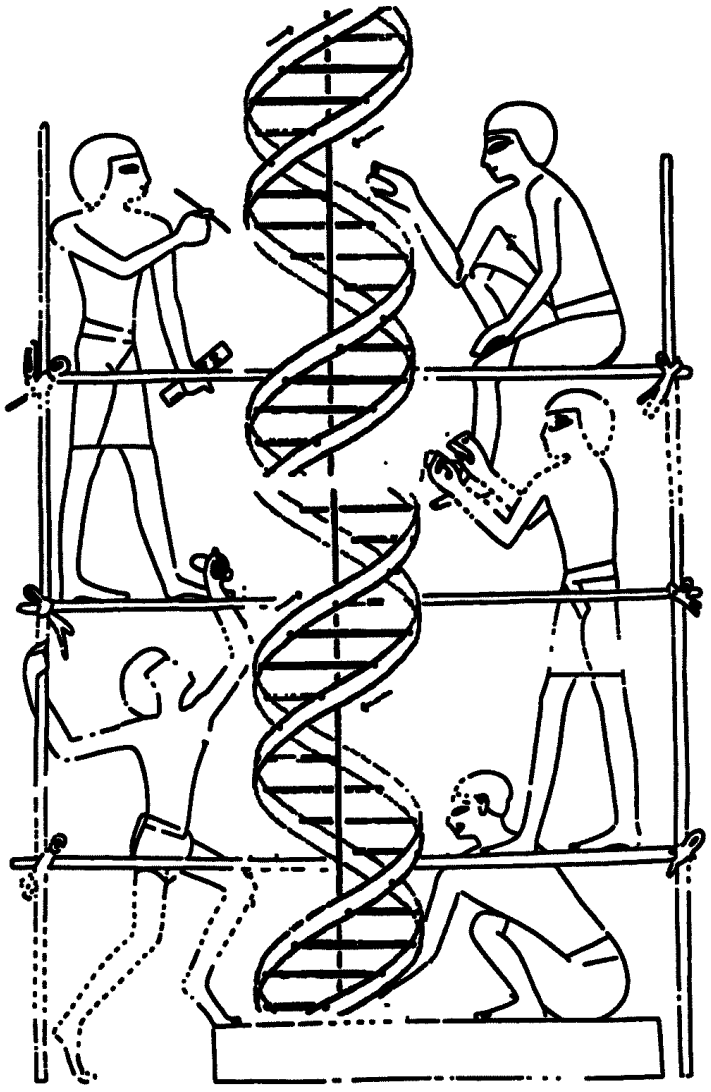
Modeling & Design of Molecular Materials 2012

Wrocław, Poland – September 10-14, 2012



Conference information & abstracts

Modeling & Design of Molecular Materials 2012

a meeting organized by

Molecular Modeling & Quantum Chemistry Laboratory
Wrocław University of Technology (WUT), Wrocław, Poland

NSF Interdisciplinary Center for Nanotoxicity
Jackson State University, Jackson, MS, USA

Charles University in Prague, Czech Republic

Wrocław Center for Supercomputing and Networking (WCSS)

Conference website: www.mdmm.pl/2012

an event sponsored in part by

Institute of Physical & Theoretical Chemistry
Wrocław University of Technology (WUT), Wrocław, Poland

Department of Chemistry
Wrocław University of Technology (WUT), Wrocław, Poland

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Conference program

September 10, 2012 (Monday)

15:00-21:00	Registration - lobby of building A-1, Wyb. Wyspiańskiego 27

September 11, 2012 (Tuesday)

8:00-9:00	Registration (continued)
9:00-9:10	Conference opening - Aula on the first floor of building A-1
Session 1	**Advances and applications of computational methods** (chair: A. Toro-Labbé)
9:10-9:40	**L1:** A. Laganà (Perugia, Italy) *Cooperative modeling and design on the computer grid*
9:40-10:10	**L2:** T. Wesołowski (Genève, Switzerland) *Revealing the bonding pattern from the molecular electron density using single exponential decay detector (SEDD): an orbital-free alternative to the electron localization function (ELF)*
10:10-10:40	**L3:** W. Grochala (Warszawa, Poland) *Molecules and solids that refuse to exist*
10:40-11:10	**L4:** Z. Latajka (Wrocław, Poland) *Xenon compounds - theoretical studies and the nature of bonding*
11:10-11:25	Coffee break
Session 2	**Modeling molecular materials** (chair: M. Yáñez)
11:25-11:55	**L5:** T. Clark (Erlangen, Germany) *From molecules to devices: modeling "soft" electronics*
11:55-12:25	**L6:** B. Szyja (Münster, Germany) *Mechanochemical bond breaking by MD simulation*
12:25-12:55	**L7:** A. Michalak (Kraków, Poland) *Theoretical study in the dehydrogenation of ammonia borane by transition metal complexes for fuel cell applications*
12:55-15:00	Lunch break

Session 3 **Modeling interactions in molecular materials** (chair: T. Clark)

15:00-15:30 **L8:** M. Yáñez (Madrid, Spain)
Modulating chemical properties and forming new materials through non-covalent interactions

15:30-16:00 **L9:** J. Murray (Cleveland, USA)
σ-hole bonding and beyond

16:00-16:30 **L10:** J. Koča (Brno, Czech Republic)
Recent progress in computational chemistry of protein/carbohydrate interactions

16:30-16:50 **L11:** M. Mitoraj (Kraków, Poland)
Non-covalent interactions from an ETS-NOCV perspective

16:50-17:10 **L12:** M. Jabloński (Toruń, Poland)
Theoretical insight into the nature of the intermolecular charge-inverted hydrogen bond

17:10-17:30 Cofee break

17:10-19:00 Poster session A (P1-P45) - lobby of building A-1

September 12, 2012 (Wednesday)

Session 4 **Advances and applications of computational methods** (chair: J. Sauer)

9:00-9:30 **L13:** A. Tachibana (Kyoto, Japan)
Chirality and stress tensor of electron

9:30-10:00 **L14:** A. Toro-Labbé (Santiago de Chile)
Towards a theory of chemical reactions and reaction dynamics

10:00-10:30 **L15:** P. Politzer (New Orleans, USA)
The Reaction force constant: some observations

10:30-10:50 **L16:** J. Jaque (Santiago de Chile)
Synchronicity in chemical reactions: a reaction force constant analysis

10:50-11:05 Coffee break

Session 5 **Modeling molecular materials** (chair: Z. Latajka)

11:05-11:35 **L17:** J. Sauer (Berlin, Germany)
Towards predictions of energies and free energies for molecule-surface interactions with chemical accuracy

11:35-12:05 **L18:** B. Kuchta (Marseille, France)
Numerical design of new porous open carbon frameworks (OCF) for hydrogen storage

12:05-12:35 **L19:** O. Shishkin (Kharkov, Ukraine)
Topology of intermolecular interactions as basis for analysis of structure and properties of molecular crystals

12:35-12:55 **L20:** A. Sikorski (Warszawa, Poland)
Diffusion in a crowded environment: simulation within the frame of the dynamic lattice liquid (DLL)

12:55-15:00 Lunch break

15:00-15:20 Panorama Art Gallery show

15:30-17:30 Wrocław sightseeing with a guide

17:30-19:00 Centennial Hall Discovery Center show and Japanese Garden

19:15-22:15 Conference Dinner

September 13, 2012 (Thursday)

Session 6 **Modeling biomolecules** (chair: N. Richards)

9:00-9:30 **L21:** W. Minor (Charlottesville, USA)
Experiment and modelling: competitive or complementary approaches to structural biology ?

9:30-10.00 **L22:** J. Polański (Katowice, Poland)
Mining molecular databases for fragonomics based exploration of the architecture of drugs

10.00-10:30 **L23:** J. Gu (Shanghai, P.R. China)
Electron attachment to biomolecules: from nucleobase to DNA

10:30-11:00 **L24:** P. Paneth (Łódź, Poland)
An MP2-based extention of chlorine isotope effects limits; challenge for the experiment

11:00-11:15 Coffee break

Session 7 **Modeling biomolecules** (chair: P. Paneth)

11:15-11:45 **L25:** J. Burda (Prague, Czech Republic)
Study on the ruthenium(II) and platinum(II) complexes and their interactions in cellular environment

11:45-12:15 **L26:** J. Korchowiec (Kraków, Poland)
Molecular modeling studies of model monolayers

12:15-12:35 **L27:** P. Dominiak (Warszawa, Poland)
Electron density and electrostatic properties of biomacromolecules from a database of pseudoatomic densities

12:35-12.55 **L28:** D. Rutkowska-Żbik (Kraków, Poland)
Theoretical modeling ofchlorophyls and their derivatives as potential therapeutic agents

12:55-13:15 **L29:** Ł. Pepłowski (Toruń, Poland)
Molecular dynamics studies of synaptic adhesion neurolignin/neurexin complexes

13:15-15:00 Lunch break

15:00-17:00 Poster session B (P46-P91) - lobby of building A-1

Session 8 **Workshop - computer laboratory 50 in building A-2** (chair: W. Bartkowiak)

17:00-20:00 **L30:** R. Zaleśny and R. Góra (Wrocław, Poland)
Computational methods to determine electric dipole properties of molecules and their aggregates

September 14, 2012 (Friday)

Session 9 **Modeling biomolecules and drug design** (chair: W. Minor)

9:00-9.30 **L31:** N. Richards (Gainesville, USA)
Computing and evaluating absolute free energy differences for protein loop conformational changes

9:30:-10:00 **L32:** J Grembecka (Ann Arbor, USA)
Structure-based development of small molecule inhibitors for acute leukemia

10:00-10.30 **L33:** T. Cierpicki(Ann Arbor, USA)
Challenges in structure based design of protein-protein interaction inhibitors

10:30-11:00 **L34:** S. Filipek (Warszawa, Poland)
Recent structures and novel activation mechanisms of GPCRs

11.00-11:15 Coffee break

Session 10 **Modeling materials and biomolecules** (chair: J. Burda)

11:15-11:40 **L35:** P. Cysewski (Bydgoszcz, Poland)
Color predictions from first principle quantum chemistry computations

11:40-12:05 **L36:** T. Kuliński (Poznań, Poland)
Structural adaptation in nucleic acids-protein functional complexes studied by computational methods

12:05-12:25 **L37:** Z. Futera (Prague, Czech Republic)
Reaction mechanism of Ru(II) piano-stool complexes; QM/MM study

12:25-12:45 **L38:** D. Plewczyński (Warszawa, Poland)
MetaDock: enzyme substrate identification using protein-ligand docking

12:45-13:05 **L39:** S. Rai (Hyderabad, India)
Electronic structure based insights into proline tagged with gold nano clusters

13:05 Conference closing

MDMM 2012 conference posters

No.	Presenting authors	Title
P1/A	Thilo Bauer Tim Clark	*SAMs on α-Al_2O_3(0001): Chemical bonding of linker groups and thermodynamic stability of surface structures*
P2/A	Joanna Bednarska Wojciech Bartkowiak Robert Zaleśny	*On the polarity of electronic excited states of photochromic molecules*
P3/A	Mateusz Brela Artur Michalak	*Molecular modeling of the alkaline anionic exchange membranes for Fuel Cells.*
P4/A	Katarzyna Brudnik Jerzy T. Jodkowski	*Theoretical study on kinetics of the abstraction of chlorine atom from chloromethanes by atomic chlorine*
P5/A	Katarzyna Brudnik Jerzy T. Jodkowski	*Halogen bonding* versus *hydrogen bonding. A computational study on three-center four- electron model systems*
P6/A	Tomasz G. Buchała Szczepan Roszak	*Modeling of heterocyclic complexes – precursors of conducting polymers*
P7/A	Vladimir Chashchikhin	*Modelling the structure and band shapes of the absorption and emission spectra of fluorescein adsorbed on the surface of mesoporous silica MCM-41*
P8/A	Marta Chołuj Joanna Bednarska Robert Zaleśny Wojciech Bartkowiak	*On the importance of atomic polarizability in polarization of medium-sized molecules*
P9/A	Piotr Cysewski	*Pi-electron delocalization as descriptors of spectroscopic properties of anthraquinones in polar mediums*
P10/A	Andrzej Drabarek Szczepan Roszak	*Localization of spin density in carbon nanotubes*
P11/A	Pavlo O. Dral Tim Clark	*UNO–CI calculations of electronic transitions in nanosystems*
P12/A	Piotr Durlak Zdzisław Latajka	*Ab initio molecular dynamics study of the very short and symmetrical O-H...O hydrogen bonds in the condensed phases*
P13/A	Karol Dyduch Mariusz P. Mitoraj Artur Michalak	*ETS-NOCV description of σ-hole bonding*
P14/A	Svetlana Emelianova	*Modeling of functional layers microstructure for organic light-emitting diodes and calculation of its properties*
P15/A	Ivelina Georgieva Natasha Trendafilova	*DFT modeling, UV-Vis and IR spectroscopic study of acethylacetone-modified zirconia sol-gel materials*
P16/A	Pablo Jaque	*Study on the hydration of the redox couple Fe^{3+} | Fe^{2+} in gas-phase*

P17/A	Soledad Gutiérrez-Oliva Jane S. Murray Peter Politzer Alejandro Toro-Labbé	*Use of the reaction force and the reaction force constant to understand the isomerization of HCN to CNH*
P18/A	Tomasz Jeliński Piotr Cysewski	*Color prediction of anthraquinones by means of first principle quantum chemistry computations*
P19/A	Paweł Kadłubański Szczepan Roszak	*4,4-diphenylsulfide oxidation with hydrogen peroxide by using 2-phenyl-1,2-benzisoselenazol-3-(2H)-one and -phenyl-1,3,2-benzothiaselenazole 1,1-dioxide as catalysts – ab initio study*
P20/A	Somchai Keawwangchai Tasawan Keawwangchai	*Density functional investigation of oxo-M complexes (M= Mn, Tc and Re) with tetraazacycloalkene and tetraazacycloalkane derivatives*
P21/A	Tasawan Keawwangchai Somchai Keawwangchai	*The selective fluorescent chemosensors for Cu^{2+} ion based on BODIPY derivatives: experimental and theoretical study*
P22/A	Jan Konieczny Borys Szefczyk	*Molecular dynamics simulations of imidazolium-based ionic liquids - properties and structure at the interface*
P23/A	Justyna Kozłowska Robert W. Góra Wojciech Bartkowiak	*Influence of spatial confinement on electric properties of p-Nitroaniline*
P24/A	Andreas Krause Tim Clark	*Molecular dynamics simulations of multiphase systems: complementing experimental SHG studies*
P25/A	Ondřej Kroutil Zdenek Chval	*Immobilization of nucleosides on quartz (101) surfaces*
P26/A	Kamila Olech Szczepan Roszak	*Design of low bandgap copolymers for organic electronics*
P27/A	Alimet Sema Özen	*Peripheral and structural effects on the band gap of acceptor-donor type conducting polymers*
P28/A	Monika Parafiniuk Mariusz P. Mitoraj	*Theoretical study on mechanism of dehydrogenation of ammonia borane catalyzed by palladium complexes*
P29/A	Monika Pawłowska Teresa Żołek	*Molecular modeling as a valuable tool for the properties prediction of molecularly imprinted polymers*
P30/A	Łukasz Piękoś Artur Michalak	*Molecular dynamics of ethylene polymerization processes catalyzed by half-metallocene titanium(IV) complexes*
P31/A	Julia Romanova	*'Extended viologens': a quantum-chemical study*
P32/A	Rafał Roszak Szczepan Roszak	*Aromatic organoberyllium compounds – effect of substituent on hydrogen adsorption properties*
P33/A	Dorota Rutkowska-Żbik	*Catalytic methane aromatisation on MoO_3/ZSM-5: theoretical studies on reaction mechanism*
P34/A	Dmytro I. Sharapa Tim Clark	*Charge transfer in systems Fe-SWCNT and Fe-graphene*
P35/A	Sebastian P. Sitkiewicz Robert Zaleśny Wojciech Bartkowiak	*Physical origins of 2,2′-bithiophene dimer stability. A DFT-SAPT study*

P36/A	Daniel Smykowski Bartłomiej M. Szyja	*Theoretical study of carbon dioxide hydrogenation: reaction thermodynamics and potential intermediate products*
P37/A	Daniel Smykowski Bartłomiej M. Szyja	*Algorithm for generating random host-guest configurations: implementation as Zeobuilder module and examples of potential applications*
P38/A	Marta Sowula Wojciech Bartkowiak	*Solvent effect on the vibrational spectrum of Michlerś ketone: an experimental and theoretical investigations*
P39/A	Michał Stachów	*Structural and spectroscopic characterization of model carbon nanotubes*
P40/A	Karol Strutyński	*DFT-D method designed for graphitic systems*
P41/A	Małgorzata Wielgus Justyna Kozłowska Wojciech Bartkowiak	*Density functional theory considerations on the push-pull D-π-A anions possessing double or triple bonds*
P42/A	Nikita I. Vakula	*DFT theoretical study of interactions between Ag_n(n=1-7) clusters and alpha-quartz (001) surface*
P43/A	Nikita I. Vakula	*Structures and vibrational spectra of 1:1 and 1:2 complexes between 2-(2'-Pyridyl)benzimidazole and its 1-methyl derivative and water molecules*
P44/A	Hidetaka Yamada	*Computational investigation of the absorption of carbon dioxide into alkanolamine solutions*
P45/A	Teresa Żołek	*A computational model for selectivity evaluation of molecularly imprinted polymers*
P46/B	Katarina Baxová Jaroslav V. Burda	*Determination of Platinum(IV) reduction potential*
P47/B	Wiktor Beker W. Andrzej Sokalski	*Testing applicability of differential transition state stabilization approach and atomic multipole expansion in design of new biocatalysts*
P48/B	Ol'ha O. Brovarets' Dmytro M. Hovorun	*Molecular mechanisms of DNA point mutations induced by the deamination of adenine: comprehensive quantum-chemical study*
P49/B	Aneta Buczek	*The strength of hydrogen bonds between water and model dehydropeptides*
P50/B	Eduardo W. Castilho-Almeida	*Interaction between lignin and vegetable oil transesterification catalysts: A DFT study.*
P51/B	Janina Kuduk-Jaworska Jerzy J. Jański	*Non-empirical quantum chemical studies of carboplatin biotransformation*
P52/B	Lidia Chomicz	*8-Bromo-2'-deoxyguanosine-3'5'-diphosphate - from electron attachment to yhe O-P bond cleavage*
P53/B	Lidia Chomicz	*Mechanism of the isopropyl radical induced degradation of DNA radiosensitizer. A computational and experimental study*
P54/B	Zdenek Chval Jaroslav V. Burda	*Mechanism of oxaliplatin binding to DNA*
P55/B	Edyta Dyguda-Kazimierowicz W. Andrzej Sokalski	*Binding of the organophosphorus pesticides by phospotriesterase: insight from classical and hybrid QM/MM simulations*

P56/B	Karolina Gluza Piotr Paneth Paweł Kafarski	*Heterocyclic mono- and bisphosphonates as a novel inhibitors for Parkinson's disease treatment*
P57/B	Karolina Gluza Ziemowit Pokładek Szczepan Roszak Paweł Kafarski	*Complexation of boronic acid with 1,2- and 1,3-diols – it is not as easy as it seems to be*
P58/B	Jerzy Hładyszowski Jerzy T. Jodkowski	*Theoretical and experimental study of hydrogen abstraction from some chosen flavonoids*
P59/B	Jana Hudecová	*Vibrational optical activity spectra of organic compounds in the C-H stretching region*
P60/B	Mateusz Jędrzejewski	*Variation of the electronic polarizability on the reaction path*
P61/B	Wojciech Kołodziejczyk Jerzy T. Jodkowski	*Conformational analysis of so called "legal highs" using quantum mechanical models*
P62/B	Dominika Kowalczyk Edyta Dyguda-Kazimierowicz W. Andrzej Sokalski	*Molecular dynamics study of phosphotriesterase-malathion complexes: influence of a single mutation on the substrate binding characteristics*
P63/B	Grzegorz Krasiński	*Molecular modeling of the kinetic enzymatic resolution of phosphoroorganic compounds*
P64/B	Katarzyna Kulińska Tadeusz Kuliński	*Computational studies of new potential inhibitors of human type II inosine monophosphate dehydrogenase*
P65/B	Petra Kührová	*Force-field dependence of chignolin folding and misfolding: comparison with experiment and redesign*
P66/B	Elena Lilkova	*Modeling the structure of human interferon gamma c-termini*
P67/B	Magdalena Malik	*Which DFT Methods should we choose for predicting the molecular structures and vibrational spectra of new platinum(II) anticancer agents?*
P68/B	Karolina Mikulska	*Nanomechanics of β-rich domains proteins related to neuronal disorders*
P69/B	Przemysław Miszta Sławomir Filipek	*Theoretical study for predicting 3D structures of mosquito olfactory G-protein coupled receptors*
P70/B	Zoltán Násztor	*Influence of the Hofmeister-active salts on the interfacial properties of Trp-cage miniprotein: a computational study*
P71/B	Zoltán Násztor	*Characterizing the micelle-bound conformations of the stereoisomers of antimicrobial peptide indolicidin*
P72/B	Marzena N. Nieradka Michał Stachów	*Performance of polarization-consistent (pc-n) basis sets in predicting accurate parameters of He_2, Ne_2 and Ar_2 in the complete basis set limit*
P73/B	Ziemowit Pokładek Karolina Gluza Szczepan Roszak Paweł Kafarski	*Understanding boron atom Lewis acidity*

P74/B	Robert Ponec Pavel Beran	*Mechanism of H-H activation by frustrated Lewis pairs. Insights from the analysis of domain averaged Fermi holes and generalized population analysis*
P75/B	Maciej Przybyłek Piotr Cysewski	*Optimization of analytical conditions of a fluorimetric method for the cortisol determination*
P76/B	Klaudia Radula-Janik	*Topological analysis of electron density distribution in molecules containing a N_2O_2 functional group*
P77/B	Irena Roterman-Konieczna	*Structural form for early stage in protein folding process simulation*
P78/B	Joanna Sarzyńska Tadeusz Kuliński	*Recognition of dsRNA by HYL1 and DRB4 proteins from molecular modeling and molecular dynamics simulations*
P79/B	Parvesh Singh	*A molecular dynamics study of lunasin peptide*
P80/B	Rafał Szabla Robert W. Góra	*Molecular mechanisms of the photostability of 2-aminooxazole – a plausible RNA precursor on early Earth*
P81/B	Rafał Szabla Robert W. Góra	*The mechanism of phosphate catalysis of 2-aminooxazole formation in prebiotically plausible conditions*
P82/B	Filip Šebesta Jaroslav V. Burda	*Binding $Pt^{IV}(dach)Cl_4$ to GMP and followed-up reduction of platinum leaded to formation of $Pt^{II}(dach)Cl_2$*
P83/B	Dariusz Toczek Szczepan Roszak	*Theoretical studies of calcium polyphenol glycosides interaction*
P84/B	Natasha Trendafilova Ivelina Georgieva	*Molecular modeling of bioactive coumarins and their metal complexes*
P85/B	Elżbieta Walczak Tadeusz Andruniów	*Rhodopsin cavity impact on retinal derivatives absorption properties*
P86/B	Katarzyna Walczewska-Szewc	*Extending the range of FRET - the Monte Carlo study of the antenna effect*
P87/B	Roksana Wałęsa	*Solvent effects on the conformational preferences of model peptoids*
P88/B	Marc de Wergifosse	*Predicting and interpreting the second-order nonlinear optical responses of fluorescent proteins: a challenge for quantum chemistry?*
P89/B	Łukasz Wolański Tadeusz Andruniów	*What zeroth-order Hamiltonian for retinal chromophore CASPT2//CASSCF and CASPT2//DFT calculations?*
P90/B	Łukasz Wolański Tadeusz Andruniów	*On applicability of multiconfigurational perturbation theory to study spectral properties of GFP chromophore models*
P91/B	Marie Zgarbová	*Refinement of force field torsion parameters based on inclusion of conformation-dependent solvation effects – glycosidic torsion in nucleic acids*

Lecture abstracts

in chronological order

Cooperative modeling and design on the computer grid

Antonio Laganà

Department of Chemistry, University of Perugia, Perugia, Italy

The community

Computational Chemistry, Molecular Science and Technology researchers study the properties of matter referable to the properties of systems made of nuclei (considered as stable, though structured, entities and electron as well as of (from weak to strong) aggregates of atoms and molecules. The purpose of these studies is to invest the knowledge developed in this way to build new science, innovation, technologies and services for social and economic growth.

Accordingly, the engagement of the community in computation is addressed to a series of research activities, computer codes (either commercial or in-house implemented), database construction and management, data rendering and virtual reality handling. These activities are fragmented into a large number of laboratories that occasionally concur to carry out advanced modelling and simulations based on multi-scale and multi-physics approaches to reality starting, whenever is appropriate, from the nano-scale level.

Common applications

This means that there is already a large number of running applications the may serve a large number of users. Among them we can quote the highly successful quantum chemistry packages (like GAMESS, Gaussian, Molpro, CASSCF, NWChem, CRYSTAL etc.), which are at present solid foundations of any determination of molecular structures and properties, Molecular Dynamics packages (such as VASP, NAMD, Espresso, Gaussian'03, Gaussian'09, CHARMM, CPMD, GAMESS, GROMOS, GROMACS and Amber) and other suites of codes simulating complex realities like atmospheric reentry, the production of secondary atmospheric pollutants, materials design, photo-assisted processes, spectroscopic analytic studies etc.. With the advent of the grid more and more of these studies are being implemented on it and are becoming "flagship applications" although for most of them the natural computational platforms are supercomputers.

A cooperative service approach

Codes made available to the COMPCHEM users are increasingly being structured also as services within the blocks of the so called Grid Empowered Molecular Simulator (GEMS) [1]. To this end various tools and frameworks have been created. Among them Grif [2] is the framework allowing the optimization of the allocation of the jobs on the Grid, Gcres [3] is the tool utilizing the evaluations made by Grif to assign credits to the community members whose Quality of Service (QoS) is high. Within this effort a tool for accessing high performance supercomputers from the grid is also under development.

Acknowledgements: Support from EGI-Inspire is acknowledged.

[1] Costantini, A.; Gervasi, O.; Manuali, C.; Faginas Lago, N.; Rampino, S.; Laganà, A. *Journal of Grid Computing* **2010**, 8(4), 571–586.
[2] Manuali, C.; Lagana', A. *Future Generation of Computer Systems* **2011**, 27(3), 315–318.
[3] Manuali, C.; Lagana', A. *Lecture Notes Computer Science* **2011**, 6784, 397–411.

Revealing the bonding pattern from the molecular electron density using single exponential decay detector (SEDD): an orbital-free alternative to the electron localization function (ELF)

Piotr de Silva[1,2], Jacek Korchowiec[2], Tomasz A. Wesołowski[1]

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We introduce a new tool (Single Exponential Decay Detector - SEDD) [1] to extract the information about bonding and localization in atoms (see Fig . 1), molecules (see Fig . 2), or molecular assemblies. The practical evaluation of SEDD does not require any explicit information about the orbitals. The only quantity needed is the electron density (calculated or experimental) and its derivatives up to the second order.

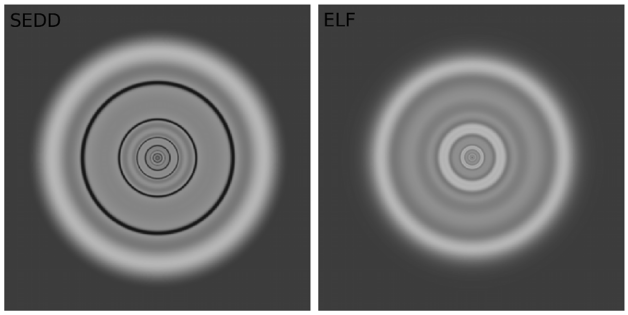

Fig. 1: SEDD (left) and ELF (right) for Xe.

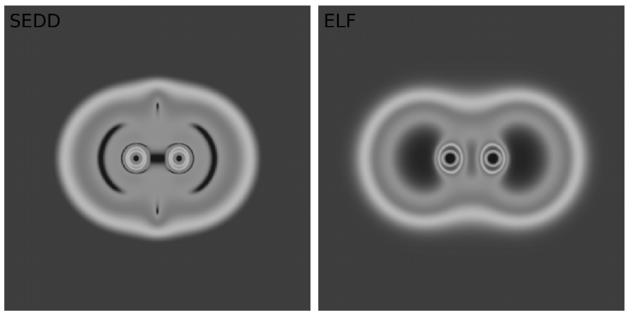

Fig. 2: SEDD (left) and ELF (right) plots for N_2.

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[1] P. de Silva, J.Korchowiec, T.A. Wesolowski, *ChemPhysChem* **2012**, *accepted*

Molecules and solids that refuse to exist

Wojciech Grochala[1,2]

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The core business of chemistry is manufacturing of novel interatomic connections. Hence, even simple stoichiometries which "refuse" to be prepared (and despite numerous efforts), distract the skilled experimental chemists. In such case, theory may be of great value to predict (meta)stability of such systems, define (p,T) conditions needed for them to survive, and suggest synthetic routes.

There are many stubborn, as-yet unknown "simple" molecules and solids "waiting to be made" [1]. Here we will discuss two cases, one from molecular (HeO) [2] and another from the solid state world ($AgCl_2$) [3].

It turns out that the singlet state of the HeO molecule may be stabilized as a local minimum at the He-O separation of ca. 1.1 Å in the presence of appreciable electric field, for example coming from a point charge (the $F^{\breve{}}$ in the $F^{\breve{}}$...HeO anion) or from two adjacent local dipole moments (such as LiF molecules in $(HeO)(LiF)_2$, see Figure 1) [2], in a similar fashion to electric field effects which are operative in the active sites of many enzymes [4]. $(HeO)(LiF)_2$ constitutes the first neutral system containing chemically bound helium atom, where all ground vibrational levels sit inside the potential energy well.

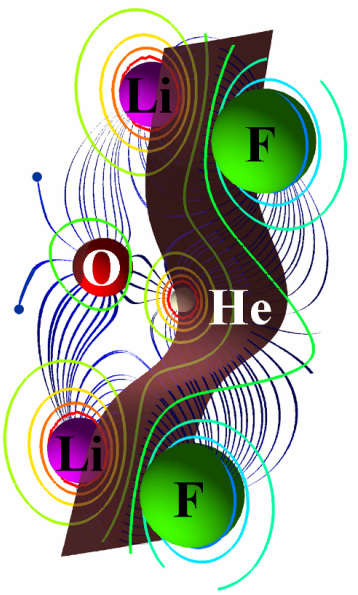

Fig. 1: Electrostatic potential of the hypothetical $(HeO)(LiF)_2$ molecule.

And what is wrong with $AgCl_2$? Solid of this stoichiometry has never been prepared despite that fact that it is isoelectronic to well known $CuCl_2$ and $AuCl_2$ as well as to AgF_2 (all related compounds are quite stable). According to our calculations [3] $AgCl_2$(s) should be thermodynamically stable with respect to $AgCl_{(s)}$ and $\frac{1}{2}$ $Cl_{2(g)}$ at $T < +13^oC$. $AgCl_{2(s)}$ should exhibit a range of unusual electronic and magnetic properties and its synthesis is now being targeted in our laboratory.

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Xenon compounds – theoretical studies and the nature of bonding

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

The first chemical compound containing noble gas atom, $Xe^{+}[PtF_6]^{-}$, was experimentally prepared 50 years ago. The last four decades have introduced a rich and interesting world of noble gas chemistry.

Recently, a new class of noble gas containing molecules, HNgY (where Y – an electronegative group), have been prepared and characterized in the low-temperature matrices spectroscopy [1]. Usually molecules are experimentally prepared in low-temperature matrices by photodissociation of a hydrogen containing precursor and thermal mobilization of the photo-detached hydrogen atoms.

In order to understand the nature of chemical bonds in the molecular systems containing Ng atoms we have applied the topological analysis of the electron localization function (ELF), which is an indirect measure of the probability of finding two electrons with the opposite spins. Via ELF analysis we can obtain information on the degree of ionic and covalent bonding in studied systems. The results of ab initio calculations, the topological analysis of the ELF and the discussion of the nature of chemical bonds with Ng atoms will be presented for following systems:

- HNgCN and HNgNC (Ng = Ar, Kr and Xe),
- HXeOHand HXeSH,
- $(HXeH)_n$ with n = 2 – 4, $Xe_2H_3^{+}$,
- FXeSiF,
- $HXeOH...H_2O$ and $XeH_2...H_2O$ (example of dihydrogen bonds);
- $HXeBr...CO_2$. (HXeBr is stable up to 100 K [2]).

Acknowledgements: Support from the National Center for Research and Development of Poland (grant ERA-CHEMISTRY-2009/01/2010). Calculations were performed at the Wrocław Center for Networking and Supercomputing.

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From molecules to devices: modeling "soft" electronics

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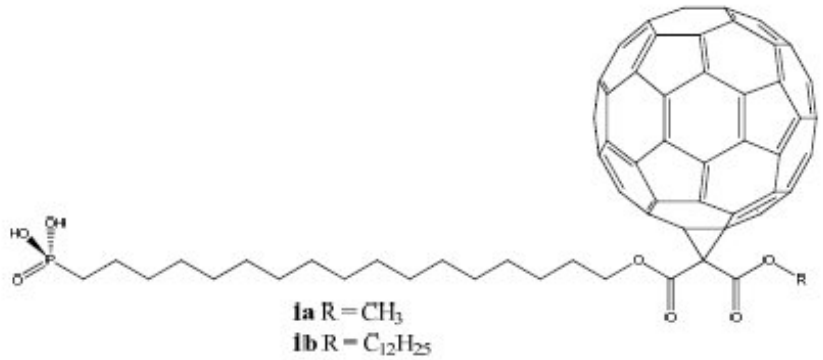
Molecular electronics promises to replace traditional silicon-based devices in many applications in which price, flexibility and low power consumption are important. Transistors based on functional self-assembled monolayers offer the advantage of very easy fabrication and low power consumption. Because the self-assembled monolayers consist of flexible organic molecules, it is important to take their dynamics into account when simulating their structures and electronic properties. Classical molecular-dynamics simulations provide a picture of the time-resolved structure of the monolayers that is consistent with experimental observations on real transistors in which both the dielectric and the semiconductor functions are assumed by molecules of type **1**. Functional devices are obtained using mixed SAMs that include approximately 75% of the unsubstituted molecules **2**.



In order to simulate the electronic properties of such monolayers, we need to be able to perform quantum mechanical calculations on tens of thousands of atoms. The new semiempirical molecular orbital program EMPIRE has been designed from scratch to be able to treat very large systems (up to 100.000 atoms) on massively parallel (thousands of CPUs) supercomputers. This program makes it possible to calculate the acceptor energy level (local electron affinity) of snapshots taken from the molecular-dynamics simulations in order to simulate the electronic characteristics of the Self-Assembled Monolayer Field-Effect Transistors (SAMFETs).

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Mechanochemical bond breaking by MD simulations

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Mechanochemical activation of chemical reaction is usually less known than thermochemical, electrochemical or photochemical ones. However, the history of mechanochemistry reaches the ancient Greek and extends to present times with Atomic Force Microscopy technique and Quantum Chemical simulations. The range of applications of mechanochemistry is quite broad, and is not limited to activating the covalent bonds mechanically. Mechanochemically induced phase transitions under high pressure as well as magnetization upon milling or unbinding and unfolding pathways for biomolecules are barely the few examples.

In this work we present the Molecular Dynamics simulations with the DFT method to investigate the influence of the artificial force in the chemical bond breaking. One example system is breaking of the coordination bond between the Ag and C atoms in the silver(II) carbene system. Simulations have been carried out using modified version of SIESTA code.

The artificial external force has been introduced by the implementation of special constraints, which added the force acting on the selected atoms along the arbitrarily selected direction. In order to prevent the system from moving, the force of same magnitude and opposite direction has been applied to the second part of the system. This is shown in Figure 1.

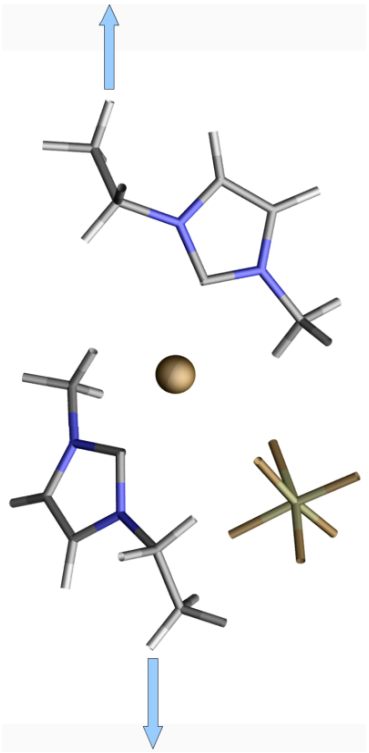

Fig. 1: Silver carbene system with forces acting on two hydrogen atoms

Along with the intuitive reorientation of the system along with the acting forces, there are other characteristic phenomena accompanying the mechanical pulling. Most important is the stretching of the bond lengths. The average bond lengths between silver and carbon atoms increase from 2.10 Å for the 0.4 nN force, through 2.13 Å for 0.8 nN, 2.16 Å for 1.2 nN, to reach 2.22 Å for the 1.6 nN force (The bond length equals to 2.06 Å in the optimized system without artificial force acting on any atoms). Depending on the force, the deformation of the system's geometry is also visible. The angles between silver-carbon-methyl decrease significantly.

The evaluation of the force needed to break the bond rise some difficulties. The experimental value of the rupture force amounts to approximately 1 nN, while MD simulation give the result between 1.6 and 2.0 nN. We need however to keep in mind the time scale of the simulation with respect to the experiment. As we mentioned before, we have simulated only 10 ps of the life of the system, whereas 1 μs is the timescale of the experiment, which is 5 orders of magnitude longer. As a rule of thumb, we could expect the force to be lowered by approximately 15-25%, which is closer to the experiment, nevertheless our model is not fully consistent with real structure, i.e. simulations have been done in gas phase, not in the solvent; the aliphatic chains at N1 position of imidazole are much, much shorter.

Acknowledgements: The computational grant from NCF is gratefully acknowledged. Calculations have been carried out at SARA on *Huygens* supercomputer.

Theoretical study on the dehydrogenation of ammonia borane by transition metal complexes for fuel cell applications

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The catalytic dehydrogenation of ammonia borane (AB; NH_3BH_3) has attracted attention because of its relatively high hydrogen storage capacity (19.6 wt% H_2). To develop efficient on-board hydrogen storage materials, a high-performance dehydrogenation catalyst for AB is needed to facilitate fast hydrogen release of maximum amounts of H_2 at low temperatures.

The main goal of the present research was to determine by theoretical calculations the mechanistic details of the dehydrogenation of ammonia borane (AB, NH_3BH_3) catalyzed by Pd(II) and Ni(II) complexes with acetonitrile ligands [1]. Static DFT methods as well as Molecular Dynamics simulations were applied to investigate the possible steps in the dehydrogenation mechanism and the influence of the solvent and the entropic factors; bonding in the reaction intermediates was characterized by the ETS-NOCV scheme.

The results allowed us to propose the full, novel mechanism of the AB dehydrogenation with Ni and Pd catalysts with acetonitrile ligands, confirmed later by experimental data. In particular, the effect of the acetonitrile ligands has been rationalized as far as the mechanistic steps, and the changes in activity of Ni and Pd under different conditions are concerned. Here the entropic and the solvent effects allowed to rationalize the activity differences. Further, a possibility of alternative mechanisms involving more than one AB molecule attached to the metal was eliminated.

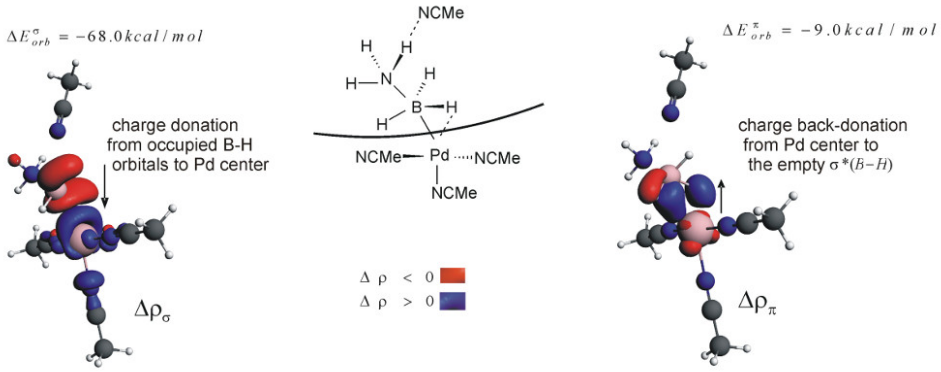

Fig. 1: Donation and back-donation channels obtained from the ETS-NOCV method for the bond between AB and the catalyst for the most stable complex.

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Modulating chemical properties and forming new materials through non-covalent interactions

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Non-covalent interactions are fundamental in chemistry and in nature, because they are responsible for the organization of practically all molecular assemblies, of natural origin like DNA, or of artificial origin as the so-called metal-organic-frameworks (MOFs), or "soft matter", term usually employed to describe materials that are held together by non-covalent interactions involving energies of the order of the thermal energy, kT. Many of these non-covalent interactions involve a Lewis base and a Lewis acid, but although the concepts of Lewis acidity and basicity are almost one century old, the rationalization of the strength of the interactions is not a trivial matter. In many cases the deformation of one of the interacting units (or of both of them) plays a fundamental role in the strength and nature of the interaction [1,2]. Also importantly, the intrinsic reactivity of many chemical compounds, can be modulated, or even dramatically changed through non-covalent interactions [3]. In some other cases these interactions can be almost as strong as conventional covalent bonds, leading to the formation of new stable materials, as the metallocycles formed by the interaction of unsaturated organic compounds with Cu halides [4]. Non-covalent interaction may also influence each other when present in the same chemical system, leading to cooperative effects resulting in the stability enhancement of both of them. This is the case of the interaction of beryllium bonds with both inter- and intramolecular hydrogen bonds [5]. In same cases the competition between these two kinds of bonds, results in the displacement of the latter by the former, justifying the named sometimes assigned to be as the "tetrahedral proton".

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σ-hole bonding and beyond

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σ-Hole bonding is a highly directional noncovalent interaction between a localized region of positive electrostatic potential on a covalently-bonded atom of Groups IV – VII and a negative site [1], e.g. the lone pair of a Lewis base. The positive electrostatic potential is due to the anisotropic charge distribution of the Group IV – VII atom, which shows depletion of electronic density (a σ-hole [2]) on the extension of the bond to the atom. When the σ-hole is on a Group VII atom, the interaction is labeled halogen bonding. σ-Hole complexes usually have binding energies of less than about 12 kcal/mol. However for negative sites with relatively loosely-held electrons, the interaction may develop a degree of coordinate covalency, with considerably stronger bonding [3]. An analogue of σ-hole bonding is π-hole bonding. A π-hole is a localized region of positive electrostatic potential perpendicular to a molecular framework [4]. This is found, for instance, above and below the sulfur in SO_2. Examples of various types of σ-hole and π-hole interactions will be discussed.

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Recent progress in computational chemistry of protein/carbohydrate interactions

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We have more and more information indicating that protein-carbohydrate interactions are involved in many biological processes including cell signaling and/or cell-cell adhesion. In order to understand and to be able to influence such processes, it is important to know all details of this kind of interactions. Computational methods may help substantially within this respect.

There are basically two types of intermolecular forces involved in protein-carbohydrate interactions. The first is represented by polar interactions mainly between the OH group of the carbohydrate and polar amino acid residues of the protein. As these interactions must compete with the interaction of the carbohydrate OH groups with water molecules in the bulk solvent, they are often enlarged by presence of ions as a bridge particle.

The second key type of protein-carbohydrate interaction is based on the interaction of a carbohydrate's apolar part with aromatic amino acid residues of the protein, known as the dispersion interaction or the CH/pi interaction. We will show in this lecture that dispersion interactions are, for some protein-carbohydrate complexes, the key interactions that can be surprisingly strong. This explains already some time known fact that reasonable amount of protein-carbohydrate complexes found in databases is based on such kind of interaction.

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Non-covalent interactions from ETS-NOCV perspective

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In the present work we will demonstrate applicability of ETS-NOCV method (combined charge - NOCV and energy decomposition scheme – ETS), in a description of, so called, non-covalent interactions. The main advantage of ETS-NOCV scheme is that it allows not only for decomposition of the deformation density, $\Delta\rho$, into the different components (such as σ, π, δ, etc.) of the chemical bond, but it also provides the corresponding energy contributions to the total bond energy. Thus, the ETS-NOCV scheme offers a compact, qualitative and quantitative, picture of chemical bond formation within one common theoretical framework.

In the present study we will comparatively characterize (i) inter and intra-molecular hydrogen (ii) halogen (iii) hydride (iv) hydride-halogen (v) dihydrogen and (vi) so called long multicenter bonds. The nature of dihydrogen ($NH^{\cdots}HB$) bonding will be discussed in the context of hydrogen storage materials. Interestingly, in all of the analyzed systems mentioned above the ETS-NOCV based results indicated significant degree of covalency (density accumulation in the interatomic region), despite the fact that they are called in the literature as "non-covalent" (for an example of intra-molecular NH...HB bonding in the analogue of cis-buthane $NH_3BH_2NH_2BH_3$ as well as in non-typical halogen bonded system NaNC—ClF, see Figure below).

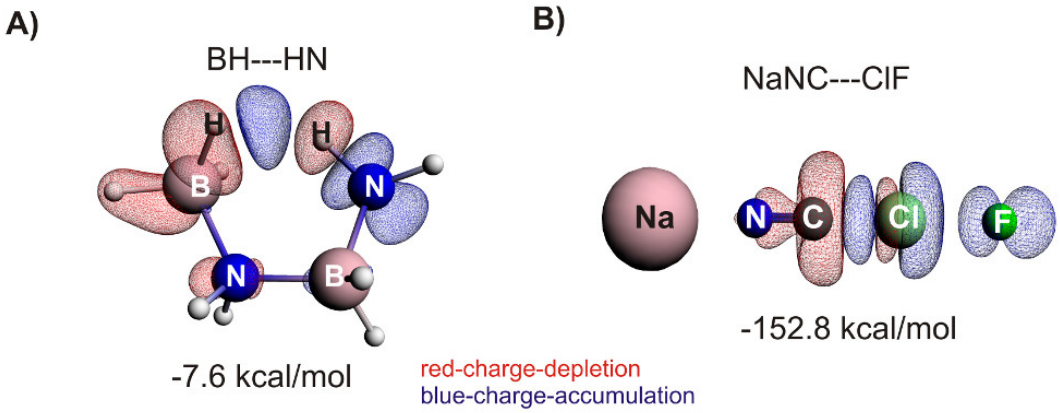

Fig. 1: The contours of NOCV-deformation density contributions describing dihydrogen NH—HB (part A) and NaNC—ClF bonding (part B). In addition the corresponding energies are shown. Outflow of electron density is marked on red color, inflow- blue color.

Theoretical insight into the nature of the intermolecular charge-inverted hydrogen bond

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Very recently we have introduced [1–3] a new type of inter- and intramolecular interaction where formally negatively charged hydrogen atom of the $X^{\delta+}$–$H^{\delta-}$ unit interacts with an atom Y possessing a lone pair vacancy, $\supset$Y, thus this interaction can be labeled as $X^{\delta+}$–$H^{\delta-} \cdots \supset$Y. Contact of this type was then called [1] the charge-inverted hydrogen bond (CIHB) to reflect the opposite 'polarization' of the hydrogen bond bridge, $X^{\delta+}$–$H^{\delta-} \cdots \supset$Y, as compared to the classical hydrogen bond with positively charged hydrogen interacting with an atom possessing an electron lone-pair, $X^{\delta-}$–$H^{\delta+} \cdots \subset$Y. Based on the NBO method it is shown [4] that the elongation of the X–H bond and the red-shift of its stretching vibration frequency are caused by the charge transfer from the bonding σ_{XH} orbital to the empty p_{z} (LP) orbital of the Y atom. Based on quantum theory of atoms in molecules (QTAIM) by Bader it is shown that the charge-inverted hydrogen bond is a closed-shell type interaction with significant contribution of covalent character. We show that charge-inverted hydrogen bonds should be investigated as a new type of interactions which are different than more common hydric/hydride (inverse) [5–7] or agostic-type interactions [8].

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Chirality and stress tensor of electron

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Energy density concept has been reviewed here in terms of stress tensor in general relativity. Electron spin vorticity has been hidden in the energy-momentum tensor and plays a significant role in the dynamics of electron. The time-evolution of the electron spin is driven by the antisymmetric component of the electronic stress tensor through the vorticity. This is called the quantum electron spin vorticity principle. The electron spin torque is counter-balanced by the zeta force, a gradient force of the chiral electron density, whose origin is manifest in the principle of equivalence in general relativity. Symmetric component of the electronic stress tensor drives tensorial energy density of chemical reactivity.

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Towards a theory of chemical reactions and reaction dynamics

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We present few theoretical elements that are used to characterize the mechanism of chemical reactions, putting together this parts should lead to a Theory of Chemical Reactions and advance towards the formulation of a Reaction Dynamics Spectroscopy based on the reaction force [1, 2] and the reaction electronic flux (REF) [3]. The basic idea is to provide conceptual and computational tools aimed at controlling chemical reactions and makes them the subject of chemical design. In this presentation, chemical reactions will be pictured as a sequence of elementary steps (one or more) which are characterized by structural and electronic activity, a collection of fundamental chemical events, namely, bond strengthening/formation and bond weakening/breaking, these events are identified and rationalized through the reaction electronic flux. With the aim of validating the theory, different types of chemical reactions will be analyzed, their mechanism will be elucidated and the exact role played by the chemical species involved in the reaction and by external, chemical and/or physical, agents will be determined. These reactions include coupled electron proton transfer reactions involving single and double proton transfer in model systems and in DNA bases and hydrogen activation reactions in the context of the search of clean energy sources. Important issues that will be addressed in this presentation are the characterization of the physical nature of activation energies, the quantification of the energetic cost associated with the electronic activity taking place in the course of the reaction, the ability of the REF to characterize the nature of a reaction mechanism as concerted or step-wise, the control of the energetic flow taking place among the chemical fragments involved in the reaction and the building of energetic profiles based on experimental bond energy data.

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The reaction force constant: some observations

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The reaction force F(ξ) is the negative gradient of the potential energy of a chemical process along the intrinsic reaction coordinate ξ. The minimum and maximum of F(ξ) provide a natural partitioning of the process into reactant, transition and product regions: in the first and third of these, the focus is upon structural changes, in the second it is upon electronic effects [1,2]. The second derivative of the potential energy is the reaction force constant, κ(ξ) [3]. It is negative throughout the transition region, not only at the classical transition state. This is consistent with experimental work which indicates that there is a region of unstable, transient states between the activated reactant and the activated products [4]. The form of κ(ξ) in the transition region can provide considerable insight into the mechanism of the process.

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Synchronicity in chemical reactions: a reaction force constant analysis

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Earlier work, both experimental and computational, has drawn attention to the transition region in a chemical reaction, which includes the traditional transition state but extends along the intrinsic reaction coordinate ξ from perturbed forms of the reactants to perturbed forms of the products. The boundaries of this region are defined by the minimum and maximum of the reaction force $\mathbf{F}(\xi)$, which is the negative gradient of the potential energy $V(\xi)$ of the system along ξ. The reaction force constant $\kappa(\xi)$ has been recently introduced within this framework; it is the second derivative of $V(\xi)$. $\kappa(\xi)$ is negative throughout the transition region. We have demonstrated that the profile of $\kappa(\xi)$ along the transition region can be considered as a suitable indicator of synchronicity in a bond-breaking and bond-forming reaction. When the bond-breaking and bond-forming are fully or nearly fully synchronous, one $\kappa(\xi)$ minimum is found in the transition region, whereas two $\kappa(\xi)$ minima are observed when they are considerably nonsynchronous. In the latter type of reaction, a concerted mechanism takes place in two stages. In this presentation, we discuss two types of processes: double proton transfer and Diels-Alder reactions.

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Towards predictions of energies and free energies for molecule-surface interactions with chemical accuracy

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Hybrid calculations [1] that combine MP2 on cluster models with DFT+dispersion on periodic models (plus ΔCCSD(T) corrections) yield binding energies of organic molecules on (simple) metal oxide surfaces with chemical accuracy. Examples are the binding of CO and CH_4 on Mg(001) [2], of H_2, CH_4, CO and CO_2 on the internal surfaces of metal organic frameworks (MOF), [3–5] as well as the adsorption and conversion of hydrocarbons in zeolites. The importance of accurate calculations of zero-point vibrational energies is stressed. The situation is less favorable for pre-exponentials of adsorption constants and reaction rate constants, i.e. the entropy part of free energy differences.

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Numerical design of new porous open carbon frameworks (OCF) for hydrogen storage

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In recent years, a great emphasis has been placed on replacing fossil fuels with clean, renewable energy for use in vehicles. One potential solution is the use of hydrogen gas as a fuel source to power a fuel cell. For vehicular use, the US Department of Energy (DOE) has identified major challenges to implementing a hydrogen-powered which include design hydrogen storage systems capable of delivering a driving range of hundreds of kilometers. Mechanism of hydrogen adsorption in carbon porous structures is a fundamental problem for these applications.

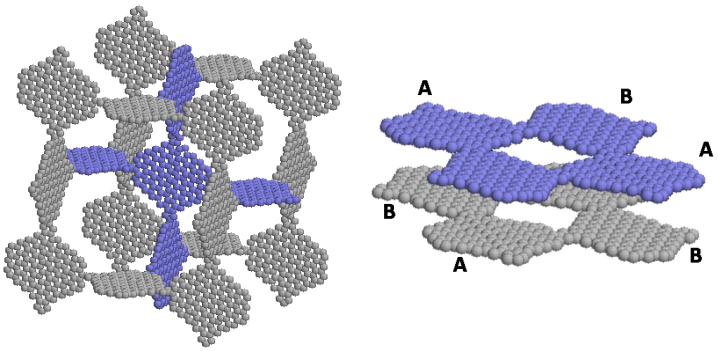

Fig. 1: New structures of Open Carbon Framework (OCF).

It can be shown that it is not possible to increase hydrogen storage capacity only by modification of slit geometry without simultaneous increase of the specific surface. So, we have introduced structures with higher surfaces and analyzed their adsorption properties. These new models of hypothetical structures represent ordered carbon structure with low density architecture required for effective application of porous carbons for mobile storage. We call them Open Carbon Frameworks (OCF). Theoretically they may have the specific surfaces exceeding 6000 m^2/g.

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Topology of intermolecular interactions as basis for analysis of structure and properties of molecular crystals

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Common approach to description of crystal structure of molecular crystals is based on analysis of distances between atoms of neighboring molecules in order to determine possible intermolecular interactions like hydrogen or halogen bonds, stacking interactions etc. Taking into account high accuracy of modern X-ray diffraction studies this method allows in most cases to find the strongest intermolecular interactions describing of crystal structure as packing of strongly bonded molecules. However, in the case of absence of such more or less strong interactions such geometrical approach is almost completely useless and structure of crystal may be described in some arbitrary way depending on aesthetic view of specific investigator.

Much more rigorous way for analysis of supramolecular architecture of molecular crystals is based on accurate calculations of intermolecular interaction energies between basic molecule located in asymmetric part of unit cell and all molecules belonging to its first coordination sphere [1–3]. Analysis of preferred pattern of crystal packing includes two steps namely i) determination of dimers formed by basic molecule with two the highest interaction energy and ii) recognition of infinite basic structural motif (BSM) containing the most strongly bonded dimers. Taking into account fixed positions of molecules in crystal values of pairwise intermolecular interaction energies have properties similar to vectors namely directionality from one molecule to another and length which is proportional to energy. This allows replacing molecules in crystal by their energy-vector diagrams or hedgehogs of intermolecular interactions. Analysis of packing of such hedgehogs easily provides information about basic structural motif of crystal.

Application of this method to crystals of hydrocarbons and their heterocyclic analogues provides clear recognition of BSM namely layers and columns where energy of intermolecular interactions of basic molecule with neighbors within this fragment is considerably higher than to molecules belonging to other such fragments. This allows describing supramolecular architecture of molecular crystals in unambiguous way as packing of strongly bonded layers or columns even in the case of existence of hydrogen bonded or stacked dimers, for example, in crystals of polymorphic modifications of the 3,4-diamino-1,2,4-triazole or derivatives of phenanthroline.

Recognition of basic structural motif of molecular crystals allows finding bridge between crystals organization and their physical properties. First of all this concerns mechanical properties. It was found that crystals undergoing shearing and bending deformations caused by specific columnar architecture of crystals.

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Diffusion in a crowded environment: simulations within the frame of the dynamic lattice liquid (DLL)

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A simple model of lateral motion in a membrane is presented. We perform extensive and systematic simulation studies of two-dimensional fluid motion in a complex crowded environment. In contrast to other works we focused on cooperative phenomena that occurred where the motion of particles takes place in a dense system [1]. Our main goal was to answer the following question: how do fluid molecules move in an environment that has a complex structure and assuming that motion of fluid molecules is highly correlated. The dynamic lattice liquid (DLL) model, which can work with the highest fluid density, was employed [2]. It became the basis for a parallel algorithm, which took into account coincidences of attempts of elementary molecular motion resulting in local cooperative structural transformations. Within the frame of the DLL model we considered cooperative motions of fluid particles in an environment that contained static obstacles. We studied the dynamic properties of the system like the mean square displacement, the relaxation time of position as a function of the concentration of obstacles. The changes of hydrodynamic interactions were also investigated by studies of the distribution of cooperative loop length. The subdiffusive motion of the liquid in the matrix of immobilized obstacles was found [3]. It was shown that the percolation threshold calculated from the dynamic behavior of the liquid molecules is considerably higher than that determined from the cluster analysis.

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Experiment and modeling: competitive or complementary approaches to structural biology?

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The three-dimensional structures determined by X-ray crystallography play a central role in understanding protein-small molecule and protein-protein interactions at the molecular level. Each unique structure deposited to the Protein Data Bank (PDB) increase the number of models that can be calculated (predicted) for experimentally unknown structures. The experimental verification of models produced by the CASP competition shows that top experts can accurately predict the overall structure of proteins when there is a similar protein of known structure and in some cases even when a protein is not similar to any protein with a known structure. However, the experimental verification of applicability of automatic methods developed for meta-servers shows that the accuracy of a predicted model significantly drops when the sequence similarity between the model and an experimentally derived structure drops below 30%.

Protein 3-D structures have long been used to search for new drug targets, but only a fraction of new drugs coming to the market were developed with the use of structure-based drug discovery method. The *in silico* screening of potential ligands is much less successful than prediction of native protein structures. The combined approach of experimental and computational methods will lead to a dramatic increase of accuracy of computational screening. Thus our understanding of protein-ligand and protein-protein interactions and our understanding of the molecular foundation of human diseases and thus leading to a high-output structure-based drug discovery system.

Mining molecular databases for fragonomics based exploration of the architecture of drugs

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Nowadays compounds are available in enormous population for commercial in vitro and in silico HTS procedures; e.g., ten million compounds are available for laboratory screening, while activity annotated databases provide access to million of real and/or virtual structures. Thus, we need novel methods for HTS (Q)SAR data handling, screening, analyzing, modeling, clustering or visualizing. Discovery informatics in this filed is a goal. The so-called knowledge discovery approaches allows today not only for the analysis of the simple problems but for the better understanding of the complex molecular architectures, e.g., this of chemistry [1]. In this context, a number of new concepts appeared recently to analyze and describe drug architecture, e.g., structure-activity landscapes, privileged structures, polypharmacology, etc. [2, 3] We will briefly discuss this and analyze a place of drugs within the architecture of chemistry.

We have developed a novel and unique molecular and structural database managing system, MoStBioDat, available as a public domain package (www.chemoinformatyka.us.edu.pl) for the analysis of large ligand libraries. MoStBioDat is not only the dual purpose storage/extraction database platform maintaining the high-standards of data integrity and reliability, but consistent environment providing software-based solutions for the massive in silico protocols parallel analyzing small molecule ligand and protein data. Several example of the application of this software will be presented and discussed.

The idea of preferential chemistry resembles this of drug-likeness. In turn, drug-likeness and PS concepts refer to similar problems. What are the differences between them? What we actually mean by drug-likeness in molecular design and do drug targets also have a likeness? On the other hand, identifying a preferential landscape is related to molecular fragments, substructures, superstructures, scaffolds, linkers as well as their generation, identification, statistical analyses of frequencies etc. Intuitively, fragments, substructures or privilege (sub)structures refer to some building blocks of the molecule. Preferences may include real molecules but also virtual structures or molecular motifs. Fragmental topology-activity landscapes (FRAGTAL), a new concept for encoding molecular database records into molecular descriptors for fragonomics will be presented. The retrieved database hits were subsequently applied for the molecular fragment frequency and activity analysis. The FRAGTAL method reconstructs the way in which medicinal chemists are used to designing intuitively a prospective drug structure. A representative example of the practical application of FRAGTAL will be discussed.

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Electron attachment to DNA: from nucleobases to DNA segments

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Theoretical descriptions for electron attachment to DNA subunits are extending from the nucleic acid bases to DNA segments, including biological entities such as nucleotide oligomers and duplexes of nucleotide oligomers [1].

The predictions of the electron affinities of nucleosides and nucleotides by the DFT have been verified by the subsequent photoelectron experiments. These studies validate the applications of DFT methods (such as B3LYP, M05-2X, M06-2X, with medium size basis sets) in exploring the electrons interacting with relatively larger segments of DNA.

The electron affinities of the pyrimidine nucleoside di-phosphates are found to be close to those of mono-phosphates. The contribution of the phosphate group at the 3´-position in hosting the excess electron is of vital importance. The unpaired electron density is partly spread around the 3´-phosphate. The important contribution of the phosphate at the 3´-position for hosting the excess electron is also found in the radical anion of adenosine di-phosphates. In guanine rich aqueous nucleotide oligomers, the phosphate-centered valence anion might compete with the base-centered anion. One important finding of the studies of electron attachment to nucleotides is that in aqueous solution, the electron capture ability of the bases is almost independent of the existence of a counterion.

Due to the formation of intra-strand H-bonds between the neighboring bases, the position of cytosine in the sequence of an oligomer affects the cytosine electron capture ability. Stacking between G and C in nucleotide oligomers does not have an important influence on the electron capture ability of cytosine. The ultimate electron affinity of cytosine in DNA single strands in aqueous solutions is expected to be ca. 2 eV.

Electron attachment to DNA segments may trigger either C—O bond cleavage or N-glycosidic bond break. The mechanisms for such damages in DNA have been examined.

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An MP2-based extension of chlorine isotope effects limits; challenge for the experiment

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Chlorine kinetic isotope effects (Cl-KIEs) exceeding semi-classical limits were observed in enzyme-catalyzed reactions but their source has not been yet identified. We have shown [1] that these unusually large KIEs are associated with reactions in which chlorine is the central atom that is being passed between two heavy atoms. The origin of these large values is the ratio of imaginary frequencies for light-to-heavy species (so called the temperature independent factor, TIF).

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Study on the ruthenium(II) and platinum(II) complexes and their interactions in cellular environment

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Recently, Ru(II)-piano-stool complexes were reported as promising anticancer drugs in Sadler's group [1, 2]. Replacement reactions between [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 PCM 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 kinetic description of this process was obtained and compared with similar process of the cisplatin activation.

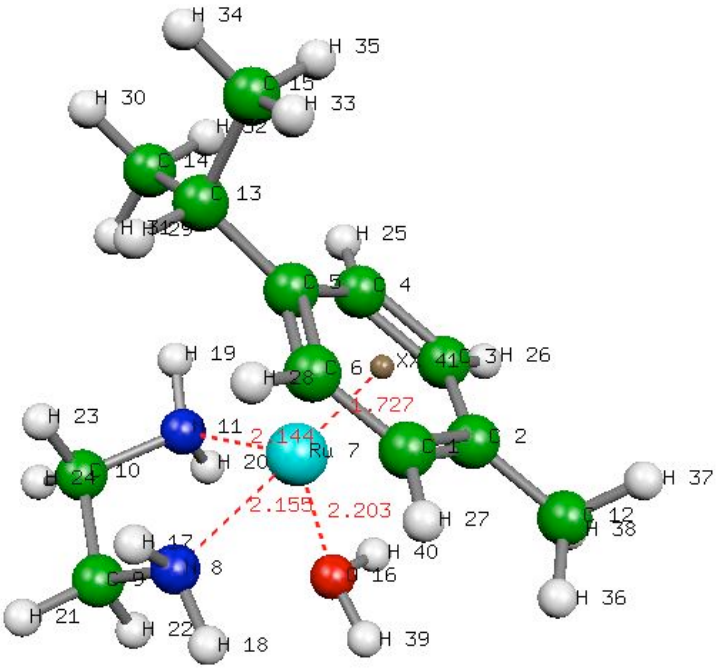

Fig. 1: General formula for the studied compounds.

Further we studied reaction mechanism of the reduction process of Pt(IV) complex. The reaction course is considered from the thermodynamic point of view. The structures were optimized at the B3LYP level with 6-31G* basis set and PCM/UA0 solvation model. The single-point energy parameters were afterwards determined at the B3LYP/6-311++G(2df,2pd) level with DPCM and scaled-UAKS solvation model developed in our laboratory recently [3].

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Theoretical study on mechanism of dehydrogenation of ammonia borane catalyzed by palladium complexes

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Monolayers are often used as model cell membranes. They are more stable compared to the native cell membranes and the physico-chemical conditions of the experiments are easily controlled. Consequently, the nature of the interactions between the molecules constituting the film can be evaluated. The situation is similar concerning the description of those systems using the molecular modeling methods. In the theoretical experiments, the composition of the system and the physicochemical conditions are fully controlled.

In this presentation the properties of monolayers are discussed. Several systems are taken into account: cholesterol/1,3-di-*O*-phytanyl-2-*O*-(β-D-maltotriosyl)glycerol (Chol/Mal3Phyt2) [1], *p-tert*-butylcalix[4]-arene-mono-propylnalidixate/1,2-dimyristoyl-*sn*-glycero-3-phospho-ethanol-amine (Calix1/DMPE) [2], and *p-tert*-butylcalix[4]arene-bis-propylnalidixate/DMPE (Calix2/DMPE), Calix1/Chol and Calix2/Chol [2]. The analysis includes pure (one component) and mixed (two component) monolayers (see Fig. 1). Atomic level information concerning the orientation of molecules and the degree of hydration of polar head groups are compared to experimental findings (surface pressure-surface potential measurements, Brewster angle microscopy and polarization-modulation infrared reflection absorption spectroscopy).

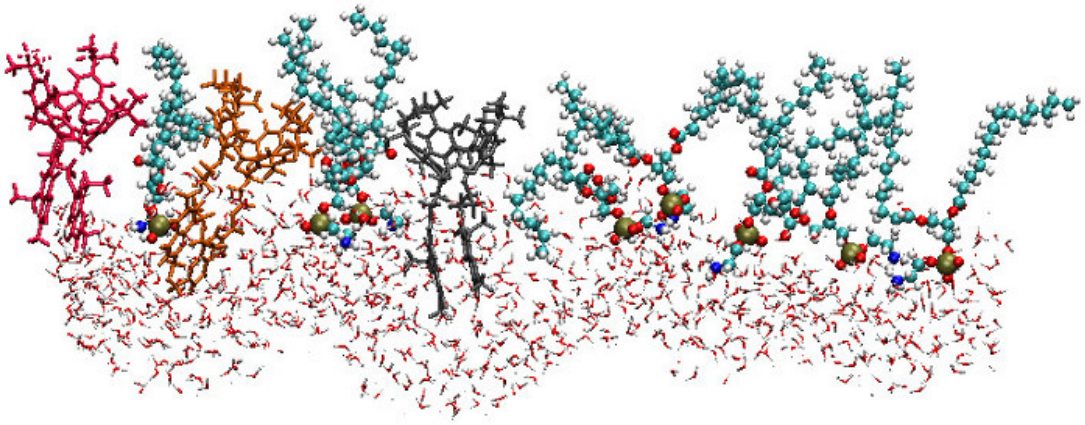

Fig. 1: Cross-sections of mixed Calix2/DMPE monolayers. The water/air interface is depicted by water molecules separated by no more than 10Åfrom surfactant molecules.

Acknowledgements: The authors acknowledge the financial support from National Science Center (Project No UMO-2011/01/B/ST4/00636).

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Electron density and electrostatic properties of biomacromolecules from a database of pseudoatomic densities

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Calculations of electrostatic properties of biomolecules or crystal energy landscapes are a particular challenge to computational chemistry. Although periodic and accurate *ab initio* methods are being developed for such calculations, they are computationally very expensive. Therefore, we face a need for alternative models, which would be quite simple and capable to describe aspherical electron density of molecules. We are developing a method [1] which allows for quantitative electron density reconstruction of organic molecules, with special emphasis put on biomacromolecules. It is based on transferability concept according to which atoms in chemically equivalent environments share similar electron density distribution. In our approach, molecular density is represented as a sum of atomic contributions (pseudoatoms):

$$\rho(\mathbf{r}) = \rho_{\mathrm{core}}(\mathbf{r}) + P_{\mathrm{valence}}\kappa^3\rho_{\mathrm{valence}}(\kappa\mathbf{r}) + \sum_{l=0}^{l_{\max}} \kappa_l'^3 R_l(\kappa'\mathbf{r}) \sum_{m=-l}^{+l} P_{lm} d_{lm}(v,\varphi), \qquad (1)$$

where the P's are the populations of the valence and spherical harmonic (d_{lm}) density functions and the κ's are radial scaling. P's and κ's, averaged over a family of chemically unique pseudoatoms, constitute the prime information stored in the pseudoatom database. A statistical analysis of these parameters is used to ensure close transferability of atomic electron densities. We have extensively verified our approach by comparing electrostatic properties of amino acids [2] and nucleic acid bases [1] derived from reconstructed densities with these coming directly from quantum mechanics computations. Our method have been already applied, among others, to analyze electrostatic contribution to inhibition of *Influenza* neuraminidase [3], zinc fingers interactions with nucleic acids and syntenin PDZ domain interactions with small polypeptides. In addition, our databank is a source of aspherical atomic scattering factors which usage improves significantly structural models derived from X-ray diffraction data [2]. In my talk, I will introduce our method, show details of method verification and present examples of applications.

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Theoretical modeling of chlorophylls and their derivatives as potential therapeutic agents

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Chlorophylls are essential functional and structural cofactors in photosynthetic pigment-proteins involved in photosynthesis. The uniqueness of their photo-physical properties is due to the extended π-electron system, what is further reflected by their electronic absorption and redox potentials. Consequently, they seek application in many fields: from medicinal chemistry to bio-sensors. The richness of their functional derivatives is achieved by varying the type of the tetrapyrrole ligand (e.g. chlorin-, bacteriochlorin- or porphyrin-type), its substituents and the central metal. The latter seems to be especially important, as the central ion influences its physico-chemical properties.

Therefore, the aim of the present contribution is to study the physico-chemical properties of chlorophylls and their selected derivatives, which might be further relevant to their possible applications. Additionally, the mechanism of synthesis of their different metallo-substituted derivatives is investigated, with focus on factors influencing chlorophyll metalation.

The reported studies are preformed within Density Functional Theory (DFT) method as implemented in Turbomole program. The GGA-BP functional with all-electron TZVP basis sets for all atoms is used. The solvation was accounted for by COSMO model with default radii for the elements, in order to take into account the nature of the possible environment in which magnesium ion is located. The bonding between the central metal and various ligands is additionally examined by SAPT(DFT) method with Molpro, to fully understand its nature.

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Molecular dynamics studies of synaptic adhesion neuroligin/neurexin complexes

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Synaptic adhesion proteins like β-neurexins and neuroligins play an important role in synapse junctions formation, maturation, and signal transduction. Mutations in genes coding these proteins occur in persons with neural diseases like autism spectrum disorders [1], Asperger syndrome, schizophrenia [2] and mental retardation [3]. The complex β-neurexin1/neuroligin1 (Figure 1) has also an important role in angiogenesis [4].

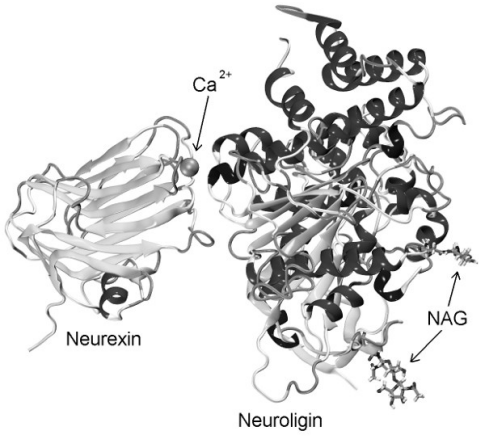

Fig. 1: A complex of β-neurexin1/neuroligin1. The Ca^{2+} ion and NAG are marked.

Herein we will present molecular details of β-neurexin1/neuroligin1 interactions obtained from a hundred nanosecond scale all-atom molecular dynamics (MD) and steered molecular dynamics (SMD) simulations of β-neurexin1, neuroligin1 and their complex (3B3Q) [5]. Trajectories in CHARMM force field [6] were analyzed and effects of Ca^{2+} ion presence at the complex interface and N-actetyl-D-glucosamine (NAG) posttranslational modifications in intermolecular interactions were characterized using free energy perturbation calculations and SMD approach.

Acknowledgements: This work was supported by Polish Ministry of Science and Higher Education, grants no. N202 262083.

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Computational methods to determine electric dipole properties of molecules and their aggregates

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Since the seminal papers of Ward and Orr [1,2], many follow-up studies have been undertaken to determine the non-linear optical polarization of isolated atoms or molecules using perturbation theory. However, with increasing size of analyzed molecular systems, direct summation over spectrum of unperturbed Hamiltonian rapidly becomes prohibitive. In the case of frequency-independent electric properties, the finite-field method of Cohen and Roothaan [3] may be a practical solution to overcome computational difficulties. Nowadays, many alternative approaches to determine resonant and non-resonant (non)linear optical properties are used and this workshop aims at their concise presentation with an eye towards pros and cons of their application.

The two hours of short, introductory lectures combined with the hands-on session will share a handful of experiences of how the existing software (including: GAMESS US, NWCHEM, MOLPRO, GAUSSIAN, DALTON and MOLCAS) can be used to estimate the discussed properties. Hints will also be given how to interface custom programs with these packages to obtain unsupported features. In particular, the following subjects shall be discussed:

- Separation of molecular response to external electric field into electronic and vibrational components.
- Methods to compute electronic and vibrational contributions to (hyper)polarizabilities.
- Numerical differentiation procedures and methods to control their stability.
- Interaction-induced electric dipole properties of molecular aggregates.

[1] Ward, J. F. *Rev. Mod. Phys.* **1965**, *37*, 1–18.
[2] Orr, B. J.; Ward, J. F. *Mol. Phys.* **1971**, *20*, 513–526.
[3] Cohen, H. D. ; Roothaan, C. C. J. *J. Chem. Phys.* **1965**, *43*, S34–S39.

Computing and evaluating absolute free energy differences for protein loop conformational changes

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Formyl-CoA;oxalate CoA transferase (FRC) is a bacterial enzyme that catalyzes the formation of oxalyl-CoA and formate from formyl-CoA and oxalate. This reaction is an essential element of the cellular mechanisms that generate ATP in the obligate anaerobe *Oxalobacter formigenes*, which lives in the gastrointestinal tract of humans. FRC is active as a homodimer in which the two FRC monomers adopt an unusual, "interlocked" fold, and a series of X-ray crystal structures have been reported that correspond to "snapshots" of the enzyme as it undergoes its catalytic cycle. During turnover a tetraglycine loop in the active site undergoes a series of conformational changes that allow it to not only stabilize reactive intermediates but also control substrate access and product release. Computational methods offer an approach to determining the thermodynamics and free energy barriers to motions of active site loops but enhanced sampling is required in order to overcome the "lagging" Hamiltonian problem. In this lecture I will present the results of Orthogonal Space Random Walk (OSRW) calculations on the energetics of the tetraglycine loop in FRC and a series of site-specific FRC mutants that have been kinetically characterized. Not only are the OSRW-derived free energy profiles well correlated with steady-state kinetic observations but the calculations also predicted the observed active site loop conformation in the G260A FRC mutant. The implications of these calculations for understanding the role of active site loop conformations in catalysis will also be discussed.

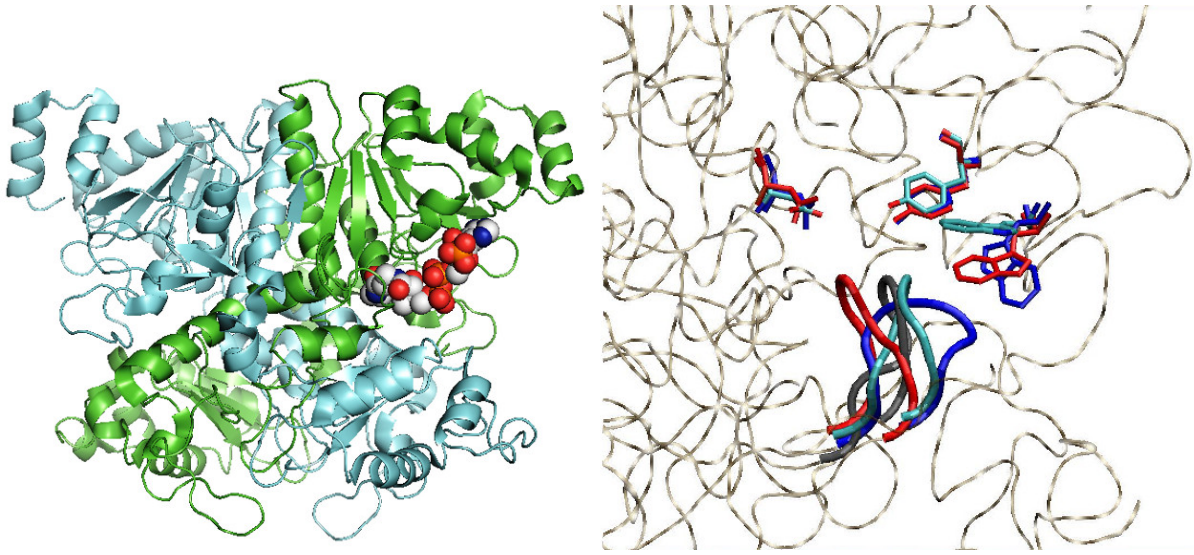

Fig. 1: (Left) Cartoon representation of the formyl-CoA transferase/CoA complex, showing the location of the active site. Protein monomers are shown in green or blue ribbon representations. Bound coenzyme A is rendered in a space-filling representation. (Right) Cartoon showing superimposed active site loops for observed (2VJN) (cyan) and calculated "open" (blue), "intermediate" (black) and "closed" (red) loop conformations in the G260A FRC mutant.

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Structure-based development of small molecule inhibitors for acute leukemia

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Protein-protein interaction (PPI) between menin and Mixed Lineage Leukemia (MLL) protein plays a critical role in development and progression of acute leukemias with translocations of *MLL* gene. Patients with MLL leukemias have very poor prognosis (only 35% five year survival) demonstrating a pressing need for development of new therapies. Genetic studies have demonstrated that disruption of the menin-MLL fusion protein interaction abrogates development of acute leukemia *in vivo*, validating this interaction as an important therapeutic target in MLL leukemias. We have developed small molecule inhibitors targeting menin and inhibiting the menin-MLL interaction *in vitro* and in human cells and blocking the MLL fusion protein mediated leukemogenic transformation [1]. Recently, we have solved the high resolution crystal structure of human menin, menin-MLL and menin-ligand complexes. These structures revealed that the small molecule inhibitors we developed bind to the MLL binding site on menin and mimic the interactions of the MLL peptide with the protein. Application of structure-based designed methods, including Glide (Schrödinger) and Ludi (Discovery Studio, Accelrys), resulted in development of nanomolar inhibitors of the menin-MLL interaction with a very pronounced effect in human leukemia cells derived from patients with MLL translocations. Computational approaches have also been used to correlate experimental IC_{50} values of menin-MLL inhibitors with the calculated interaction energy of these compounds with protein residues in the vicinity of the ligand binding site, providing a good correlation and supporting SAR. Our results emphasize the importance of structural data and application of computational methods in development of potent small molecule inhibitors of PPIs with desired physicochemical properties. A combination of experimental and computational approaches applied to develop and optimize these compounds will be presented.

[1] Grembecka J. et al. *Nat. Chem. Biol. 2012*, 8(3), 277–84.

Challenges in structure based design of protein-protein interaction inhibitors

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Development of low-molecular weight compounds targeting protein-protein interactions (PPIs) is generally considered a challenging task. Because protein-protein interactions constitute highly attractive targets for drug discovery, the number of successful examples is constantly increasing. Menin is a highly specific binding partner for MLL and leukemogenic MLL fusion proteins. Disruption of the protein-protein interaction between menin and MLL fusion proteins using genetic methods blocks development of acute leukemia in mice, indicating that menin functions as a critical oncogenic co-factor of MLL fusion proteins and is require for their leukemogenic activity. The menin-MLL interaction represents an attractive therapeutic target for development of novel drugs for acute leukemias with MLL rearrangements. We have recently developed small molecule inhibitors binding to menin and disrupting the interaction with MLL [1]. In order to further develop these compounds we have determined high resolution crystal structure of menin and obtained crystal structures of complexes with small molecule inhibitors. Using the structural information we have developed very potent second-generation inhibitors, which binds to menin with low nanomolar affinities and are capable to potently inhibit the MLL-fusion protein mediated leukemogenic transformation. Using high resolution structures for multiple protein-ligand complexes we will demonstrate rationale behind designing potent compounds and emphasize the effects of water molecules and protein dynamics. Our work provides an important structural insight into the design small molecule inhibitors of protein-protein interactions.

Acknowledgements: Support from the American Cancer Society Research Scholar Grant RSG-11-082-01-DMC to T.C and Leukemia and Lymphoma Society TRP grant 6116-12 to J.G. is acknowledged.

[1] Grembecka J. et al. *Nat. Chem. Biol.* **2012**, 8(3), 277–84.

Recent structures and novel activation mechanisms of GPCRs

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G protein coupled receptors (GPCRs), also called 7TM receptors, form a huge superfamily of membrane proteins that, upon activation by extracellular agonists, pass the signal to the cell interior. Recent studies of GPCRs changed the old dogma of a simple classification of the receptor ligands into agonists, antagonists and inverse agonists. Now, it is apparent that the same ligand can play diverse roles even in the same receptor acting as an agonist or an antagonist in different signaling pathways. Biochemical and crystallographic methods together with molecular dynamics simulations and other theoretical techniques provided models of receptor activation based on the action of so-called molecular switches buried in the receptor structure [1]. The recent crystal structures of GPCRs with antagonists and especially with agonists made it possible to explain the mechanism of receptor activation and passing the signal from the ligand binding site to the G protein for some GPCRs from the best characterized family A (rhodopsin-like). However, the specificity of particular receptor types and also different behavior of the same receptor with different ligands suggest that the activation mechanism, although similar in global movements of helices, is divergent at local scales where particular switches are involved. Extra signaling via arrestin and also the possibility of allosteric modulation in receptor dimers provide additional levels of complexity in functioning of GPCRs.

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Color prediction from first principle quantum chemistry computations

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Many industrial and commercial products are to be characteristic also by their color. This important parameter requires standardization and reproducibility. However, tint perception is a complex human activity involving physical, physiological and psychological counterparts. The theory of color perception suggests that existing three channels, responding in an antagonist way, are specialized for detection of color vision with non-uniform sensitivity in short (420–440nm), middle (530–540nm) and long (560–580nm) wavelengths ranges. The existence of such three distinct cone cells stands for the principle, that three parameters are sufficient for quantification of human color sensation and stands for so called tristimulus values defining the color space. The electronic spectrum of alizarin was measured in 1:1 water-methanol solution. The pH was controlled by series of buffers between 4.0 and 7.8 with 0.2 step or by different amounts of inorganic bases such as KOH, NaOH or LiOH. The multivariate analysis of obtained spectroscopic data were first used for decomposition into additive contributions of independent components. These spectra were then used as reference data for color prediction based on first principle quantum chemistry computations. The visible part of the spectrum was modeled by different DFT functional within TD-DFT framework. The results of a broad range of functionals applied for theoretical spectrum prediction were compared against experimental data by a direct color comparison. The tristimulus model of color expressed in terms of CIE XYZ and CIE Lab parameters models was applied both to experimental and predicted spectra. It was found [1], that HSE03 method along with 6-31G(d,p) basis set provides the most accurate color prediction, much better than other commonly used functionals as B3LYP, CAM-B3LYP or PBE0.

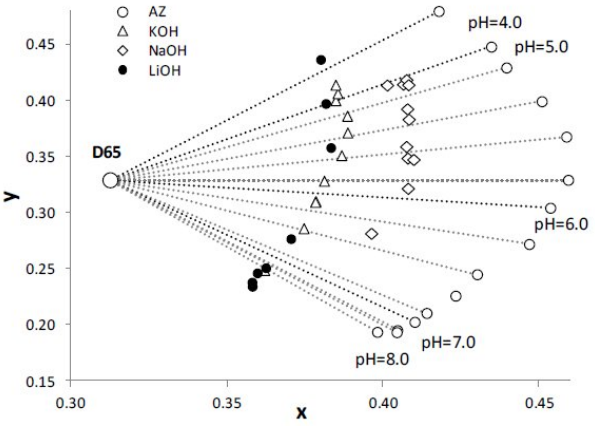

Fig. 1: CIEXYZ color space representation of AZ color in methanol modified by bases or buffers.

Acknowledgements: Results were obtained as the part of computational grant no 104 of Poznań Supercomputing and Networking Center (Poznań, Poland). The allocation of computational facilities is greatly appreciated.

[1] Cysewski, P,; Jeliński, T,; Przybyłek, M.; Shyichuk, A. *New.J. Chem.* **2012**, accepted.

Structural adaptation in nucleic acids/protein functional complexes studied by computational methods

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A fundamental step to understanding how proteins and nucleic acids function is to know there structures at the atomic level and comprehend processes of recognition. Biomacromolecules are held together with weak interactions and are easily deformed when interacting with other molecules. Studies of so called structural adaptation within functional macromolecular complexes is of importance because, can provide information on function and may be useful for rational drug design, the design of compounds that would specifically inhibit the complex and block for example viral replication. In this area, computational methods have made major contributions.

This communication will give an overview of our computational studies of structural dynamics and interactions within two examples of functionally important biomacromolecular complexes.

The formation of TAR RNA - Tat - CycT1 complex stimulates viral gene expression at the level of transcription elongation. The components of this tripartite complex do not adopt a stable fold by itself. Their structures change adaptively to optimize intermolecular interactions. TAR RNA have a rather stable double strand stem structure, while the apical loop appears highly dynamic in the absence of a ligand. The Tat protein is largely flexible in the absence of CycT1 or TAR. While some is known about how Tat interacts with the bulge region of TAR, the structural basis for TAR recognition by the full Tat-pTEFb complex, including the TAR loop, remains incomplete. In the results of MD simulations we have identified a number of dynamic modes of structural adaptation within all components of the complex, especially in the Tat/TAR recognition motif (TRM) of CycT1 and N terminal of Tat fragment, which may have implications for the mechanism of TAR binding and the formation of the full functional complex.

Our studies based on the structure of human RNase H1 complexed with an RNA/DNA hybrid give insight into HIV reverse transcription. The crystal structure of hybrid binding domain complexed with a RNA/DNA hybrid reveals that the RNA strand is recognized by a protein loop, which forms hydrogen bonds with the 2'-OH groups. The DNA interface is highly specific and contains polar residues that interact with the phosphate groups and an aromatic patch that appears selective for binding deoxyriboses. The analyses of MD trajectories provide the picture of structural transformations within the complex and the dynamics of interactions.

Acknowledgements: Support from grants No. MNiSW - N N519 405037 is acknowledged. Calculations were performed at the Poznań Supercomputing and Networking Center and with PL-Grid Infrastructure.

Reaction mechanism of Ru(II) piano–stool complexes; QM/MM study

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Biologically relevant interactions of piano–stool ruthenium(II) complexes with *ds*-DNA are studied by QM/MM computational technique. The whole reaction mechanism is divided into three phases — hydration of $[Ru^{II}(\eta^6\text{-benzene})(en)Cl]^+$, consequent binding DNA and final intra–strand cross–link formation between two adjacent guanines. Free energy profiles of all reactions are explored by QM/MM MD umbrella sampling approach where the Ru(II) complex is described by DFT. For that purpose, special QM/MM software was developed to couple Gaussian and Amber programs. Calculated free energy barriers of Ru(II) hydration as well as DNA binding process are in good agreement with experimentally determined rate constants. Reaction pathway for cross–link formation was predicted that is feasible from both thermodynamic and kinetic point of view.

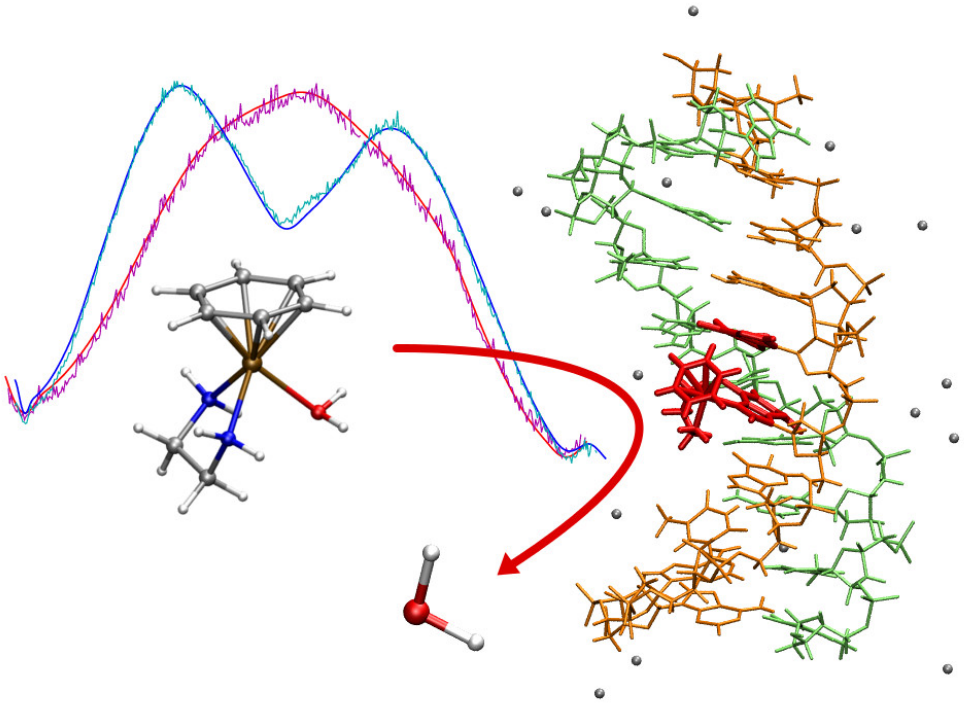

Fig. 1: Fundamental reaction of Ru(II) piano–stool complexes — binding to DNA, specifically to N7 nitrogen of guanine base. Two reaction pathways are considered.

MetaDock: enzyme substrate identification using protein-ligand docking

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[*]Contributed equally

The rapid growth in the number of known proteins, yet without experimentally appointed biological function, make molecular docking algorithms valuable in silico enzyme function identification tool. Recently, several research groups have been evaluating this approach extensively, especially in the identification of a given enzyme native substrates [1–3]. The benchmark studies show that apparently searching for native substrates in many enzymes datasets is still the challenging task.

The aim of MetaDock docking procedure is to predict correct poses of substrates within a binding site of the protein as well as to score them according to the strength of interaction in a reasonable time frame. The purpose of our studies was to present the novel consensus approach to predict both protein-substrate complex structure and its corresponding binding affinity. Our method used as the input the results from seven docking programs (Surflex, Glide, GOLD, eHiTS and AutoDock) that are widely used for docking of ligands.

Here, we perform extensive cross-docking experiments on the dataset comprising non-redundant *Escherichia coli* enzymes, for which the three dimensional structure is known, against known substrates, when docking into their corresponding enzymes, and secondly to highly score cognate substrates that are similar to the native ones. The aforementioned procedure was investigated for different classes of molecules, and diverse set of physic-chemical features describing selected substrates. Finally, we analyzed for each enzyme – both the binding affinities, and three dimensional complex structures for 10 best ranked molecules.

Encompassing the docking space within a strictly limited grid around the active site improves proper substrate ranking. Even if metabolic docking protocol fails to assign good ranking for its native substrate, often the high position is assigned to small chemical molecule with high similarity in regard to cognate ligand. We observe that large and hydrophilic substrates recognize their native enzymes more often than small, hydrophilic ones.

Acknowledgements: The calculations were performed in the Interdisciplinary Center for Mathematical and Computational Modelling (ICM) at Warsaw University under the computational grants G49-19, G14-6 and G30-2.

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Electronic structure based insights into proline tagged with gold nano clusters

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Interaction between metal nanoparticles and biomolecules is important from the view point of developing and designing biosensors. Proline tagged with gold nanoclusters is studied using density functional theory (DFT) calculations for its structural, electronic and bonding properties. [1] Geometries of the complexes are optimized using the PBE1PBE functional and mixed basis set, i. e., 6-311++G for the amino acid and SDD for the gold clusters. Equilibrium configurations are analyzed in terms of interaction energies, molecular orbitals and charge density. Time dependent DFT calculations are also carried out to investigate the non linear optical (NLO) properties. The complexes associated with cluster composed of odd number of Au atoms show higher stability. This is confirmed by larger magnitudes of HOMO-LUMO gap and excitation energies. Major components of interaction between the two moieties are (a) the anchoring N-Au and O-Au bond and (b) the non covalent interactions between Au and N-H or O-H bonds. Using NBO and AIM programs effective charge transfer interactions between amino acid and gold cluster are analyzed. All the studies indicate that the nature of interaction between the two moieties is partially covalent.

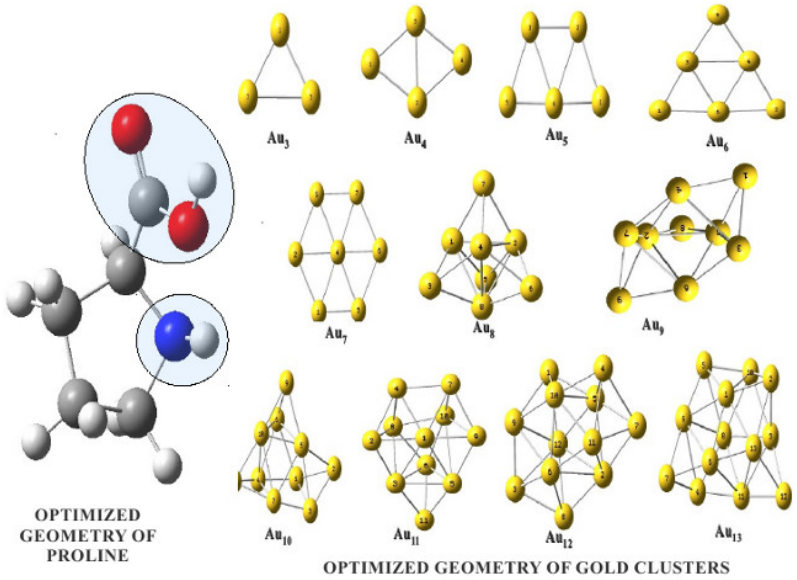

Fig. 1: Proline interaction with gold clusters(Au3-13).

Acknowledgements: Support from CSIR award No. 09/917(0006)/2010-EMR-I is acknowledged. Calculations were performed at the International Institute of Information Technology.

[1] Rai, S.; Kumar, N. V. S.; Singh, H. *Bull. Mat. Sci.* **2012**, *in press*.

Poster abstracts

in alphabetical order of the leading author's last name

Poster session A - September 11 (Tuesday)
Posters: P1-P45

Poster session B - September 13 (Thursday)
Posters: P46-P91

SAMs on α-Al_2O_3(0001): chemical bonding of linker groups and thermodynamic stability of surface structures

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Al_2O_3 is used in materials science as substrate for self-assembled monolayers (SAM). SAMs play an important role in the construction of novel organic electronic components such as transistors (SAM-FETs) [1,2]. Despite this promising technological use the chemistry at the monolayer-substrate interface is not completely understood. This lack in understanding hinders the purposive design of optimal substrate properties and reaction parameters. With phase diagrams based on total energy calculations we explain the linkage mechanisms of methyl phosphonic acid and methyl carboxylic acid to α-Al_2O_3(0001) surfaces. We show the dependence of chemical bonding on ambient conditions such as humidity and the dependence of SAM stability on surface structure. We comment on the possibility of α-Al_2O_3(0001) surface reconstruction from its UHV structure to the thermodynamically more stable pseudo gibbsite phase.

Acknowledgements: Computational time for this work was provided by Regionales Rechenzentrum Erlangen (RRZE) with its LiMA HPC system.

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On the polarity of electronic excited states of photochromic molecules

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Photochromic molecules receive much attention nowadays due to their interesting photophysical properties and promising applications in the field of nonlinear optics. Most extensively studied photochromic systems include azobenzenes, spiropyrans, fulgides, spirooxazines or diarylethenes, to name few families of compounds. Experimental works are often accompanied by quantum-chemical calculations. Due to the relatively large size of photochromic compounds, the most common choice is to employ the Kohn-Sham formulation of density functional theory to determine equilibrium structures, strength of one- and two-photon transitions or nonlinear optical properties. The calculations are frequently performed with an eye towards establishing structure-property relations. Since the seminal paper of Oudar and Chemla [1], few-level models derived from the perturbation theory form the quantitative basis for such analyses. A key parameter in these models is the dipole moment difference between the ground (g) and electronic excited (e) state ($\Delta\mu_{g,e}$). There are also extensions which rely on coupling of $\Delta\mu_{g,e}$ to vibrational modes [2]. Although much attention has been paid to the assessment of performance of exchange–correlation functionals in determining of one–photon spectra, thorough analysis regarding the computations of polarity of intramolecular charge–transfer excited states of photochromic compounds is yet to be performed. The present study aims at filling this gap. In doing so, we employ several exchange–correlation functionals including their long–range corrected variants. The values of $\Delta\mu_{g,e}$ computed using the CC2 and the CCSD wavefunctions serve as a reference point for the assessment purposes.

Acknowledgements: The work was financed by a subsidy from the Polish Ministry of Science and Higher Education within "Iuventus Plus" program (Grant No. 0628/IP3/2011/71).

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Molecular modeling of the alkaline anionic exchange membranes for fuel cells

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The polybenzimidazolium (PBI) hydroxides are potentially interesting compounds for the use in alkaline anionic exchange membrane fuel cells (AAEMFC). [1] Currently experimental studies are focused on possible usage of the derivatives of these systems. The main goal of the present study was to investigate by theoretical calculations the effect of introduction of the ether-groups on the geometrical and electronic structure of the cationic polymer and its interactions with anions. Monomers, dimers, and trimmers of the systems shown in Fig. 1, as well as these systems interacting with different anions (OH^-, F^-, Cl^-, I^-, HCO_3^-, BF_4^-) were investigated with static DFT calculation, as well as the Born-Oppenheimer Molecular Dynamics (BO-MD); ETS-NOCV analysis was used to characterize the interaction between ions. The results allow for rationalizing the experimental observations, concerning the stability of the systems with various ions, and indicate substantial differences in the character of bonding of OH- and other ions.

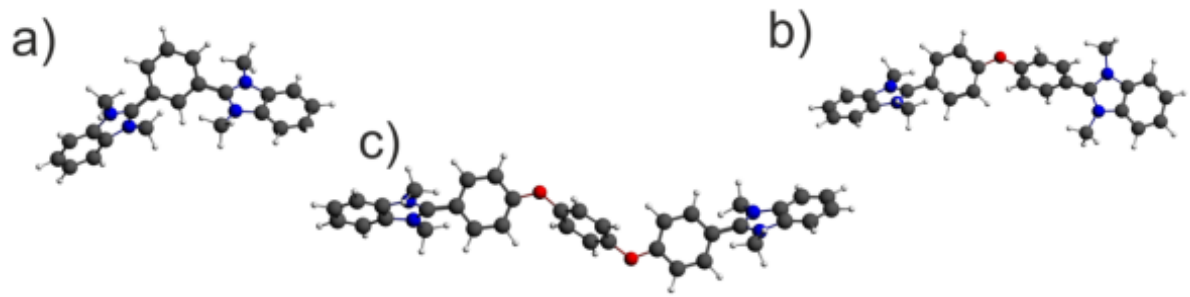

Fig. 1: Figure 1. PBI-related monomers considered in the present study.

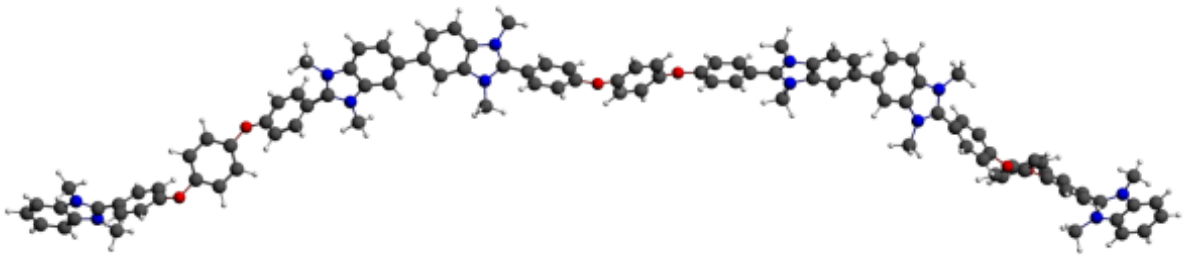

Fig. 2: Figure 2. An example of the trimer investigated in the present study (see Fig. 1c)

Acknowledgements: This research was supported in part by PL-Grid Infrastructure (ACC Cyfronet AGH).

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Theoretical study on kinetics of the abstraction of chlorine atom from chloromethanes by atomic chlorine

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Chloroalkanes and products of their environmental reactions are considered toxic and biocumulative species. The products of the atmospheric destruction of chloromethanes may be involved in various catalytic atmospheric reaction cycles responsible for the depletion of the ozone layer. Methyl chloride (CH_3Cl) is the most abundant halocarbon in the atmosphere. Major natural sources of methyl chloride are biomass burning, oceanic emissions and vegetative emissions. The other chloromethanes occurred in the polluted atmosphere: dichloromethane (CH_2Cl_2), trichloromethane ($CHCl_3$) and tetrachloromethane (CCl_4) are primarily released from industrial processes.

The reaction with hydroxyl radical is a major loss pathway for atmospheric chloromethanes, but in the marine boundary layer and polar regions, reaction with Cl atoms can also become of some importance. The sources of chlorine atoms are the photochemically labile chlorine compounds such as Cl_2 and $ClNO_2$ produced in some aqueous-phase reactions in the airborne seawater droplets.

The gas-phase reactions of chlorine atoms with the hydrogen-containing atmospheric halocarbons lead to the facile generation of the corresponding free radicals via hydrogen atom abstraction. These reactions play also an important role in the processes of industrial chlorination and incineration of hazardous halogenated wastes and their kinetics has been a subject of many theoretical and experimental studies. A considerably less recognized is the kinetics of the chlorine abstraction reactions. Therefore, in this study we present a theoretical analysis of the mechanism and kinetics of the reactions of chloromethanes, $CH_{4-x}Cl_x$ (x = 1,2,3 and 4) with atomic chlorine

$$CH_{4-x}Cl_x + Cl \longrightarrow CH_{4-x}Cl_{x-1} + Cl_2$$

and the reverse processes

$$CH_{4-x}Cl_{x-1} + Cl_2 \longrightarrow CH_{4-x}Cl_x + Cl$$

Results of ab initio calculations of the potential energy surface of the reaction systems show that the mechanism of the chlorine transfer is not elementary. The reactions studied proceed with the formation of loosely bound intermediate complexes of reactants or products. The occurrence of the intermediates implies a complex, multi-step reaction mechanism.

The theoretical description of the reaction kinetics was based on the assumption that the formed intermediate complexes are not stabilized by collisions, but at once undergo possible forward or backward processes. The values of the rate constants of the reactions studied were calculated in a wide temperature range. This has significant importance for some practical applications related with the kinetic modeling of atmospheric chemistry and combustion.

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Halogen bonding *versus* hydrogen bonding. A computational study on three-center four- electron model systems

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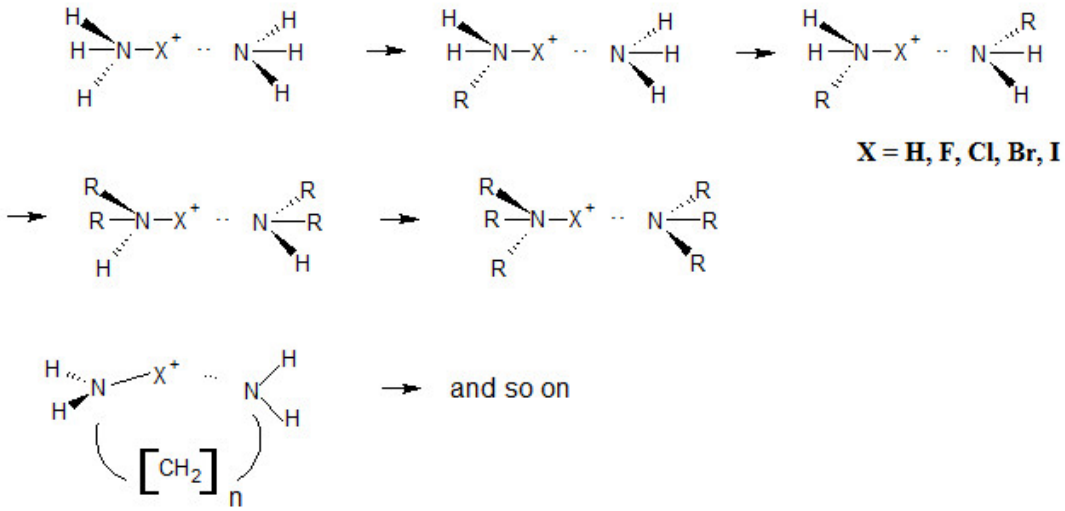

The systematic study on molecular structure and interactions were performed for ammonia and its methyl derivatives as model systems for assessment of the level of theory to be applied for larger three-center four-electron halogen-bonded species, (see Figure 1). It was observed for Py-Br(+)-Py and Py-I(+)-Py complexes that [N-X(+)-N] moiety is symmetric in solution whereas theirs hydrogen bonded counterparts are asymmetric, in general. The B3LYP Density Functional and MP2 up to CCSD(T) schemes with (aug)-cc-pv(d,t,)z Dunning' basis sets, and polarizable continuum (PCM) model of solvent treatment were analyzed in our study.

Acknowledgements: We wish to thank the Wrocław Center for Networking and Supercomputing for generous allotment of computer time.

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Modeling of heterocyclic complexes – precursors of conducting polymers

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The subject of research was polypyrrole. The following properties were tested: spin electron density, ionization energy, distribution of molecular orbitals HOMO / LUMO, the energy band gap and the formation of the conduction band in the material.

The main part of the research was focused on the pyrrole monomer and dimer. Structural properties of the monomer and pyrrole dimer for neutral molecules and their cations were observed and compared with each other. The charge distribution assigned by NBO was also investigated for understanding the concept of conductivity.

For the oligomers of the number of mers over 7 molecular orbitals HOMO / LUMO and structural features as the dihedral angle between the mers have been studied. Diagrams of the energy gap and conduction band in oligomers have also been determined.

Modelling the structure and band shapes of the absorption spectra of fluorescein adsorbed on the surface of mesoporous silica MCM-41

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The adsorption of various forms of the fluorescein dye on the surface of mesoporous silica MCM-41 was investigated using molecular dynamics (MD) methods. An atomistic model of the MCM-41 surface was built by cutting out a hexagonal pore with a diameter of 2.5 nm from an amorphous SiO_2 structure. To reduce the computational time, the obtained pore model was divided into four 700-atomic clusters with a hydroxylation degree of 2 OH groups per nm^2. Using a genetic algorithm, various structures of complexes of ionic forms of fluorescein with the surface of mesoporous silica were constructed.

Parameters for intermolecular interactions were estimated using quantum-chemical DFT calculations. MD trajectories of silica/dye complexes were calculated using the MMFF94 force field. From the calculated trajectories, the band shapes of absorption were calculated using TDDFT and TDDFT/PCM approaches. The calculated results were compared with the available experimental data. The effects of the silica substrate and the environment on the dye spectra were analyzed. The proposed approach can be used to calculate the spectra of various dye/substrate complexes.

On the importance of atomic polarizability in polarization of medium–sized molecules

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Polarizability (α) is the fundamental physical quantity which describes the response of a molecule to an external electric field and determines the optical and electrical properties of materials. Out of three contributions to polarizability (electronic, vibrational and rotational) which are related to different effects of an external electric field interaction with molecules, of the largest importance (in terms of magnitude) is the electronic one (α^{e}). In many textbooks, the vibrational contribution to polarizability is referred to as "atomic polarizability" (α^{at}) [1]. It is usually assumed that α^{at} = 15-20% α^{e}. Although the electronic contributions to polarizability have been computed for many molecules, the studies regarding the vibrational counterpart are scarcely available in the subject literature. The primary goal of our project is to calculate α^{at} and α^{e} for a selected set of molecules (polar and non-polar) to estimate the ratio of the two contributions. To achieve this goal we follow the perturbation-theoretic method of Bishop and Kirtman, employing state-of-the-art *ab initio* quantum chemistry methods.

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Pi-electron delocalization as descriptors of spectroscopic properties of anthraquinones in polar mediums

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The quantitative structure–property relationship (QSPR)-based approach is commonly used in diverse areas of chemical sciences. This led to successful predictions of many physicochemical properties very often without necessity of deep knowledge of actual mechanism or chemical structure. Also excited-state properties of organic dyes were accurately predicted using exclusively the ground-state molecular descriptors. Particularly spectroscopic properties of anthraquinones were described in terms of such descriptors as ionization potential, electron affinity, electronegativity, hardness or electrophilicity index [1]. In this project another protocol was adopted relying on the fact that chromophores responsible for color of anthraquinones are active due to $\pi \rightarrow \pi^*$ excitation. Since extend of π-electron delocalization in aromatic rings is strongly associated with this chromophore activity the aromaticity indices seem to offer quite promising set of descriptors in this particular QSPR approach. Thus, based on ground state geometry optimized using PB0/6-311++G** level series of aromaticity indices were computed and used for multi-component regression analysis. It was identified that although there is no straightforward relation between aromaticity indices of side benzene rings with maximums of absorption the central quinone ring is surprisingly accurate predictor of optical properties for analyses set of 89 anthraquinones in methanol, methanol and chloroform solutions. Quite small aromaticity of this central ring is very sensitive to the nature of side groups attached to either of benzene rings. This in turn provides linear relationships between values localization of the absorption band and such aromaticity indices as PDI, θ, TRE, pEDA or NICS(1). The rationale of this fact and areas of potential applications are discussed in details.

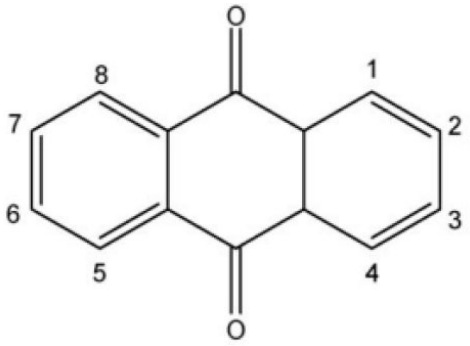

Fig. 1: Different anthraquinone derivatives were used for spectroscopic prediction based on pi-electron delocalization indices.

Acknowledgements: Results were obtained as the part of computational grant no 104 of Poznań Supercomputing and Networking Center (Poznań, Poland). The allocation of computational facilities is greatly appreciated.

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Localization of spin density in carbon nanotubes

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Chemistry of carbon nanotubes (CNTs) is a rapidly developing field of research with many potential applications in supramolecular chemistry, organic synthesis, materials science and other branches of science and technology [1].
A phenomenon of localization of spin density distribution has been predicted lately by Saloni, Roszak *et. al.* for boron-doped zig-zag CNTs of certain length [2]. It is a potential future way of controlling reactivity and adsorption properties of nanotubes.

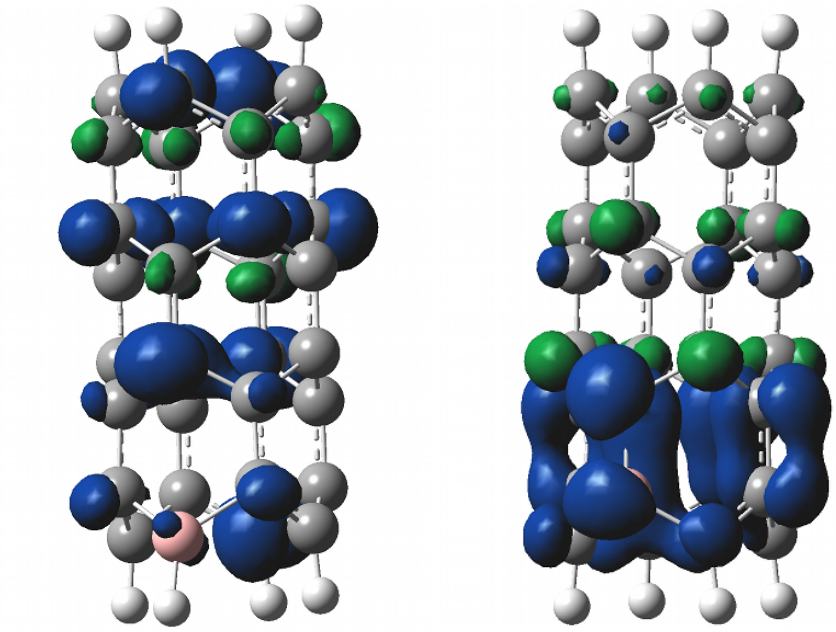

Fig. 1: Global and local spin density distributions in 4,0 B-doped CNTs (isovalue: 0.002 e)

Further study of the phenomenon has been performed by introducing additional variables to the problem, including different dopant type (nitrogen), position and nanotube length and chirality. The spin density distribution localization in its pronounced form visible in Figure 1 proved to be specific for the B-doped zig-zag structures investigated in the works of Saloni, Roszak *et. al.*, although some degree of localization is visible in all considered systems. In general, the localization effect disappears with increasing CNT length. This possibly diminishes the probability of the future practical application of this property, but further understanding of this phenomenon may shed a new light on the understanding of electronic properties and reactivity of carbon nanotubes.

Acknowledgements: Calculations were performed at the Wrocław Center for Networking and Supercomputing.

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UNO–CI calculations of electronic transitions in nanosystems

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The abbreviation UNO–CI stands for Unrestricted Natural Orbital – Configuration Interaction, i.e. configuration interaction (CI) performed in an automatically determined active space that consists of the unrestricted natural orbitals (UNOs) with significant fractional occupational numbers (SFONs between 0.02 and 1.98). UNOs (**U**) are the eigenvectors and their occupation numbers are eigenvalues of the total density matrix $\mathbf{P^T}$ (sum of α- and β-density matrices). UNO–CI was implemented in the semi-empirical MO program VAMP 11. If full CI is performed, the method is called UNO–CAS. However, in most cases it is sufficient to perform the computationally more economical UNO–configuration interaction singles (UNO–CIS). The latter method predicted optical band gaps of model compounds of different carbon allotropes (PAHs and polyynes) in very good agreement with experimental values. The accuracy of semi-empirical UNO–CI methods is comparable and even better than that of TDDFT methods, but the latter methods are computationally much more expensive and limited to much smaller systems than UNO–CI. [1]

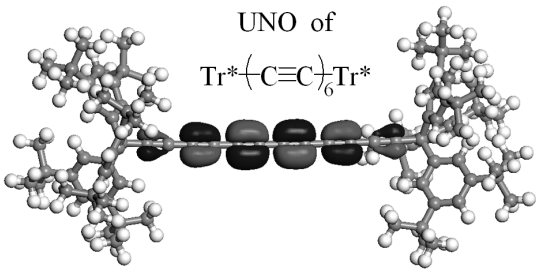

Fig. 1: Visualized highest-energy unrestricted natural orbital (UNO) of polyyne with six triple bonds

Moreover, UNO–CIS proved suitable for determining the nature of the experimentally observed charge transfer (CT) absorption bands of porphyrin-fullerene dyads [2]. In addition, experimental band gaps of metal coordination polymers were reproduced well by the title methods. Thus, semi-empirical UNO–CI methods are very reliable and fast and are very suitable for predicting and explaining electronic transition of relatively large nanosystems.

Acknowledgements: P.O.D. is very thankful to Universität Bayern e.V. for the Stipendium nach dem Bayerischen Eliteförderungsgesetz. We greatly appreciate discussion of the UNO–CAS method with Prof. Peter Pulay. The authors also thank Prof. Rik Tykwinski, Dominik Prenzel and Johanna Januszewski for the fruitful discussion of the properties of polyynes and cumulenes.

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Ab initio molecular dynamics study of the very short and symmetrical O-H...O hydrogen bonds in the condensed phases

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Theoretical studies of the structure and proton motion in the symmetrical, intramolecular and shortest hydrogen bonds yet reported in the literature. A comparison was conducted between 3-cyano-2,4-pentanedione [1] and 4-cyano-2,2,6,6-tetra-methyl-3,5-heptanedione [2] (see Fig.1) in the solid state. Dynamics of proton motion in the O-H...O hydrogen bond was investigated in NVT ensemble at 298 K and 50 K respectively for crystals using Car-Parrinello [3] and Path Integral [4] molecular dynamics. Very large delocalization of bridging proton is noted especially in Path Integral simulation where quantum effects are taken into account. Infrared spectrum has been calculated and comparative vibrational analysis has been performed. CPMD vibrational results appear to be in a qualitative agreement with the experimental ones.

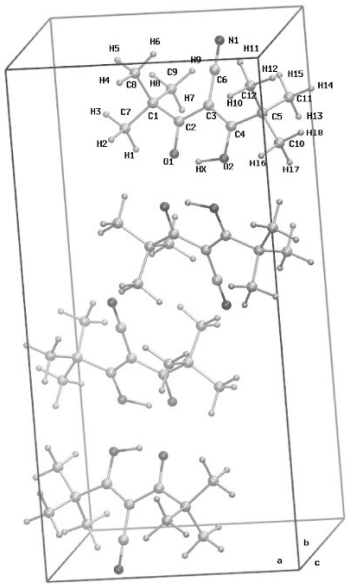

Fig. 1: The unit cell and atoms labeling of 4-cyano-2,2,6,6-tetra-methyl-3,5-heptanedione crystal.

The crystals data from the Neutron Diffraction study by Silvernail [1] and Belot [2] have been selected as starting points simulations in CPMD program version 3.13.2. Preconditioned conjugate gradient (PCG) method was used for crystal optimized. The Monkhorst-Pack mesh (2,2,2) have generated for calculated k-points in reciprocal space in each direction. Real space Ewald summation of electrostatic interactions (8 cell replicas in each direction) were employed. CPMD and PIMD (ten replicas "polymer-beads" using the normal mode variable transformation) simulations (NVT ensemble) were carried out at 298 K and 50 K respectively with a time step of 3.0 a.u. (0.072566 fs) coupled to a Nosé-Hoover chains thermostat at a frequency of 3200 1/cm. The gradient-corrected functional of Perdew, Burke and Ernzerhof (PBE) was employed. Core electrons were treated using the norm-conserving atomic pseudopotentials (PP) of Troullier and Martins, while valence electrons were represented in a plane-wave basis set truncated at an extended energy cut-off of 60 Ry. The vibrational spectrum has been also calculated using the Fourier transformation of the dipole autocorrelation function obtained from dipole trajectories generated by the CPMD simulation.

Acknowledgements: The authors would like to gratefully acknowledge the Ministry of Science and Higher Education of Poland for the support of this research; Grant No. 105/10/E-344/M/2011. Thanks also are due to the Academic Computer Center in Gdansk (CI TASK) for the use of the Galera-ACTION Cluster and the Wrocław Center for Networking and Supercomputing (WCSS) for the use of the Supernova Cluster.

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ETS-NOCV description of σ-hole bonding

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Halogen bonds, R-X···B, between a terminal halogen atoms (X) and a Lewis base (B), play a significant role in chemistry and biochemistry. Origin of halogen bonding was explained by Politzer et al. [1] based on molecular electrostatic potential (MEP); namely by the existence of positive MEP area on the outer part of X atom at the extension of R-X bond. This MEP feature was later rationalized by the σ–hole concept, i.e. a decrease in electron density resulting from R-X bond formation [2].

In the present study the ETS-NOCV analysis [3, 4] was applied to describe the σ-hole in a systematic way in a series of halogen compounds, CF_3-X (X=I, Br, Cl, F), CH_3I, and $C(CH_3)_nH_{3-n}$-I (n=1,2,3), as well as for the example germanium-based systems. $GeXH_3$, X=F, Cl, H. Further, the ETS-NOCV analysis was used to characterize bonding with ammonia for these systems. The results show that the dominating contribution to the deformation density, $\Delta\rho_1$, exhibits the negative-value area with a minimum, corresponding to σ-hole (Fig.1). The "size" (spatial extension of negative value) and "depth" (minimum value) of the σ-hole varies for different X in CF_3-X, and is influenced by the carbon substituents (fluorine atoms, hydrogen atoms, methyl groups). The size and depth of σ-hole decreases in the order: I, Br, Cl, F in CF_3-X. In CH_3-I and $C(CH_3)_nH_{3-n}$-I, compared to CF_3-I, introduction of hydrogen atoms and their subsequent replacements by methyl groups lead to the systematic decrease in the σ-hole size and depth. The ETS-NOCV σ-hole picture is consistent with the existence the positive MEP area at the extension of σ-hole generating bond, as well as with the changes in energy of the interaction with ammonia.

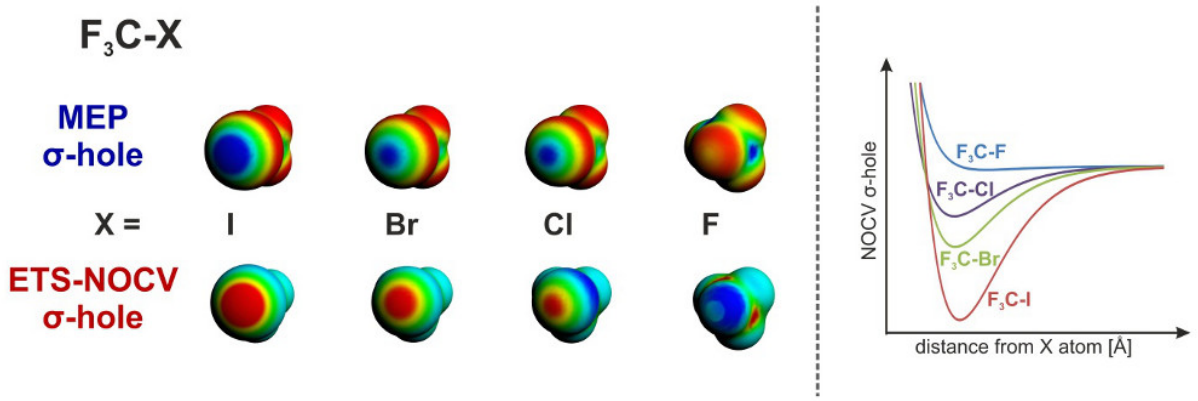

Fig. 1: Graphical representation of the σ-hole on the halogen atom, based the on MEP (upper row) and the NOCV deformation-density channel $\Delta\rho_1$ (lower row and the right-hand side plot).

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Modeling of functional layers microstructure for organic light-emitting diodes and calculation of its properties

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In the past two decades, the field of organic electronics has developed from a proof-of-principle phase into a phase of major research and development. Currently, there are a large number of materials used in organic electronics. The study of the microstructure of thin film materials is of great interest since it was found that the characteristics of materials depend largely of the morphology of the molecules in the layer.

In this work a functional amorphous layers of 1,3,4-oxadiazole (OXD), N,N'-Di(1-naphthyl)-N,N'-diphenyl-4,4'-biphenyldiamine (α-NPD) and bis(10-hydroxybenzo(h)quinolinate)berrillium (Bebq2) are studied. First, force constants for bonded and non-bonded parameters for these materials are derived based on the results of DFT calculations. AMBER [1] force field has been chosen as the basis. The appropriate structure of the amorphous layer is obtained by molecular dynamics (MD) simulations and deposition process simulations. All molecular dynamics calculations were performed using the program GROMACS [2]. To estimate molecular packing in the generated amorphous morphologies different properties and characteristics of the material were calculated.

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DFT modeling, UV-vis and IR spectroscopic study of acethylacetone-modified zirconia sol-gel materials

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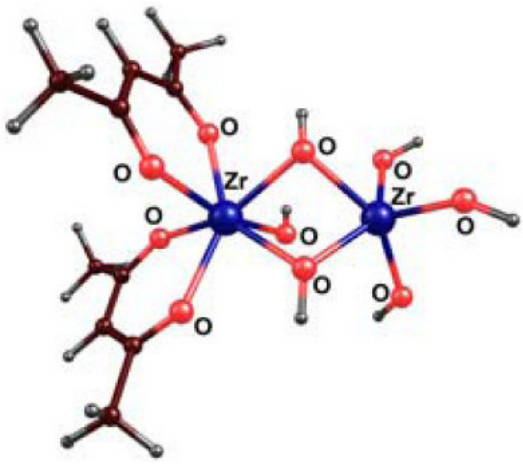
Zirconia is one of the most investigated sol-gel systems due to the excellent properties of ZrO_2 material, which have led to its use in porous membranes, matrices in catalysis, and dense dielectric and ferroelectric films in electronics. Recently, we synthesized hybrid zirconia sol-gel materials modified with acetylacetone (AcAc) and demonstrated that AcAc agent produces yellow-brown colored materials and a decrease of the optical band gap of the sol-gel zirconia from 4.84 eV to about 3 eV [1]. Despite of numerous investigations, the chemistry and the structures of Zr(IV)-AcAc complexes formed in zirconia sol and during gelation are not well understood. Theoretical and spectroscopic studies of a series of monomeric and dimeric complexes formed by the modification of the zirconium butoxide precursor with acetylacetone and subsequent hydrolysis and/or condensation have been performed applying DFT/B3LYP/6-31++G(d) and high accurate RI-ADC(2) methods. Based on model calculations and on comparison of simulated and experimental UV-Vis and IR spectra of the studied structures, the most probable building units of the Zr(IV)-AcAc gel were predicted: the dimeric double hydroxo-bridged complex $Zr_2(AcAc)_2(OH)_4(OH)_{2br}$ **9** and the mono-oxo bridged complex $Zr_2(AcAc)_2(OH)_4O_{br}\cdot 2H_2O$ **12**. In both structures the two AcAc ligands are coordinated to one Zr atom. It was shown that the building units 9 and 12 determine the photophysical and vibrational properties of the gel material. The observed UV-Vis and IR spectra of Zr(IV)-AcAc gel were interpreted and a relation between the spectroscopic and structural data was derived. The observed UV-Vis band at 315 nm is assigned to a ligand – metal/ligand transition and that at 298/288 nm - to intra-/inter AcAc ligand transition.



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Acknowledgements: Support from grant DO-02-233/2008 of the National Science Fund of Bulgaria is acknowledged. The calculations were performed at the computer cluster MADARA of Bulgarian Academy of Sciences.

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Study on the hydration of the *redox* couple $\mathbf{Fe^{3+}}$ | $\mathbf{Fe^{2+}}$ in gas-phase

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Starting from the bare metal ion, the sequential hydration of both oxidation states in the iron *redox* couple $\mathrm{Fe^{3+}}$ | $\mathrm{Fe^{2+}}$ has been studied until it reaches 6 water molecules. The conformational space for each metal–aquo–complex $[Fe(H_2O)_n]^{2+}$ (n=1–6, q=2,3) in gas phase was deeply explored using a modified Metropolis test algorithm, called ASCEC [1]. Even their different spin multiplicities were explored. All isomer generated were characterized by using DFT electronic structure calculations at the B3LYP/LANL2DZ level. It was found that the high-spin states (d^6) quintuplet and (d^5) sextuplet for $[Fe(H_2O)_n]^{2+}$ and $[Fe(H_2O)_n]^{3+}$, respectively, are the ground states for all aquo–complex, even for the bare cations. The structures of the oxidized and reduced complexes exhibit in general the same geometry except for the complexes with n =6 where it is shown that the so-called first coordination shell of Fe(II) forms an octahedral (T_h symmetry) structure while for the acidic Fe(III) (pK_a=2,2) it was found a structure of coordination number 4 with a tetrahedral arrange ($[Fe(H_2O)_2(OH^-)_2]^+$) having two hydronium ions surrounding it. This suggests that more than 6 water molecules are needed to reach the first solvation shell for Fe^{3+}. In small hydrates in gas-phase, many ions tend to organize the water molecules nearest them in a manner that substantially differs from the hydrogen-bonding network of bulk water, the effects of specific noncovalent interactions on the aquo–complex structures can be investigated individually or in combination [2]. In order to study possible effects that act on the standard reduction potentials E° of iron metal ions such as ion size, hydrolysis, and charge state, we are interested in how water molecules are interacting with different ions and how the identity of the ion affects the development of hydrogen bonding structure in successively larger solvation shells. Electronic structure properties, as well as energetics properties like binding energy, HOMO-LUMO gap, and ionization potential of all the doubly and triply charged aqua–metal complexes are also used to relate the afforded mentioned physical chemistry effects to the intrinsic standard reduction potentials $E^\circ_{Fe^{3+}|Fe^{2+}}$.

Acknowledgements: The authors acknowledge FONDECYT through the project N^o 1100291. D.Y. thanks CONICYT for a PhD fellowship.

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Use of the reaction force and the reaction force constant to understand the isomerization of HCN to CNH

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It is well known that the methanimine (CH_2NH), hydrogen cyanide (HCN) and hydrogen isocyanide isomer (CNH) are very important molecules in astrophysics, since they can act as donors and/or acceptors of protons, being this extremely important in prebiotic and extraterrestrial chemistry [1]. It was postulated that these species may have reacted in the interstellar medium to form amino acetonitrile, which is a direct precursor of glycine, the Strecker synthesis route [2] being a possible way.

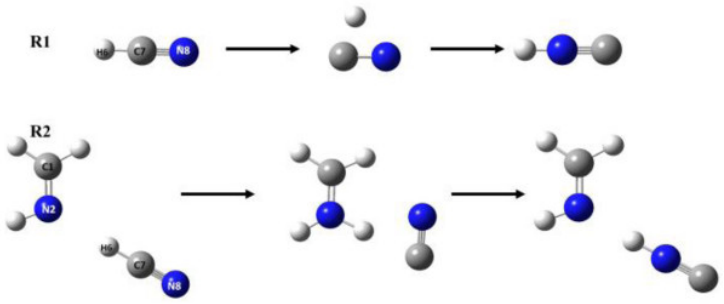

Fig. 1: Isomerization reaction of hydrogen cyanide (HCN) to hydrogen isocyanide (CNH) without and with methanimine, R1 and R2, respectively.

The isomerization reaction HCN→CNH is a crucial step in the Strecker synthesis route and it is the subject of this work. Methanimine acts as a catalyst in the isomerization reaction of hydrogen cyanide to hydrogen isocyanide and decreases the energy barrier found for the interstellar molecular change. In this work the reaction mechanisms of this specific isomerization reaction in the absence and presence of methanimine is presented (see Figure 1).

This study is based on the analysis of the profiles, along the reaction coordinate ξ, of the reaction force F(ξ) and the reaction force constant κ(ξ), the second derivative of the potential energy E(ξ) [3]. Using MP2 methodology, a complete characterization of the isomerization mechanism is obtained. This research emphasizes the power of the energy and its derivatives as a nice strategy to characterize, at different levels, the mechanism of chemical reactions.

Acknowledgements: The authors wish to thanks financial support from Project FONDECYT Grants No. 1100881 and No. 1090460.

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Color prediction of anthraquinones by means of first principle quantum chemistry computations

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Proper description of the color characteristics of a product plays an important role in commercial and industrial applications. However, it is important to remember that color perception itself is a complex phenomenon occurring in the human brain and a univocal scale is needed in order to quantify the color sensation. Based on the assumption that three parameters are sufficient for such quantification, the XYZ and CIE Lab standards were created, which makes it possible to infer actual color directly from experimental or theoretical spectrum of the visible region.

The purpose of this study was to confirm our earlier findings [1] that the deconvolution of the whole visible spectrum of a dye just by single Gaussian-like band can be sufficient for adequate color prediction in the CIEXYZ or CIELab frameworks and that accuracy of such color prediction is strongly dependent on the method used. The electronic spectra of four different anthraquinones (1,2-dihydroxyanthraquinone, 1-amino-2-methylanthraquinone, 1-aminoanthraquinone and 2-aminoanthraquinone) in methanol solution were measured and used as reference data for color prediction. The visible part of the spectrum was modeled according to TD-DFT framework with different DFT functionals. A single band approximation (SBA) model was used, which takes into account only the dominant excitation energy. This model is quite successful in color prediction in the cases when the optical activity of a compound is limited to one * excitation, as it was for the studied compounds.

A broad range of functionals was applied and the results of theoretical spectrum prediction were compared with experimental data by a direct color comparison in terms of CIE XYZ and CIE Lab tristimulus model of color. It was found that the 6-31G** basis set provides the most accurate color prediction and there is no need to extend the basis set since it does not improve the prediction of color. Different functionals were found to give the most accurate color prediction for different anthraquinones, namely: HSE2PBE functional for 1,2-dihydroxyanthraquinone, mPW1PW9 functional for 1-amino-2-methylanthraquinone, mPW1LYP functional for 1-aminoanthraquinone and M06 functional for 2-aminoanthraquinone. When considering the mean accuracy for the combined group of compounds, the B1LYP and PBE0 functionals perform best in color prediction. The obtained results confirm our earlier statements that the color prediction from first principle quantum chemistry computations via the CIE framework gives satisfactory results and can be widely applied.

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4,4'-diphenylsulfide oxidation with hydrogen peroxide by using 2-phenyl-1,2-benzisoselenazol-3-(2H)-one and -phenyl-1,3,2-benzothiaselenazole 1,1-dioxide as catalysts – ab initio study

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The theoretical studies of 4,4'-diphenylsulfide oxidation with hydrogen peroxide by using 2-phenyl-1,2-benzisoselenazol-3-(2H)-one (K1) and 2-phenyl-1,3,2-benzothiaselenazole 1,1-dioxide as catalysts (K2) (fig 1.). The transmissions states for each reaction was found and the role of the water in the reaction of 2-phenyl-1,2-benzisoselenazol-3-(2H)-one and 2-phenyl-1,3,2-benzothiaselenazole 1,1-dioxide was identified as the co-catalyst for hydrogen transfer. The calculations were performed at DFT levels of theory applying cc-pVDZ atomic basis set.

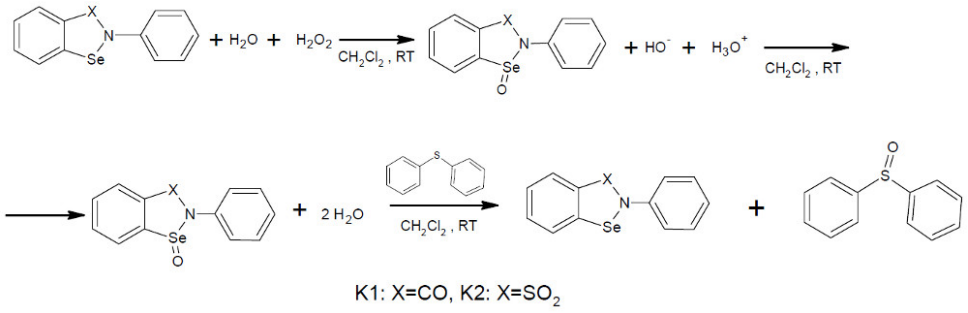

Fig. 1: 'Extended viologens' investigated in the present work.

Density functional investigation of oxo-M complexes (M= Mn, Tc and Re) with tetraazacycloalkene and tetraazacycloalkane derivatives

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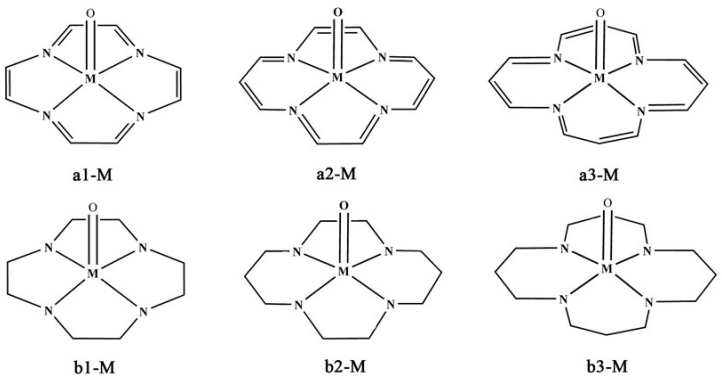

Density function calculation at the B3LYP/LanL2DZ level of theory has been performed on tetraazacycloalkene **(a)** and tetraazacycloalkane **(b)** derivatives and their complexes with oxo-M (M= Mn, Tc and Re). Electronic and thermodynamic properties of all oxo-M complexes with **a** and **b** were investigated. Structural properties of tetraazacycloalkenes and tetraazacycloalkanes have been compared. All of tetraazacycloalkenes complexes with oxo-M show more symmetric square planar pyramidal geometry than tetraazacycloalkanes complexes with oxo-M. For tetraazacycloalkene derivatives, **a1** shows the lowest binding energy with oxo-Tc (-737.93 kcal/mol) whereas **a2** and **a3** show the lowest binding energy with oxo-Mn (-721.65 and -763.73 kcal/mol, respectively). Interestingly, all of the tetraazacycloalkane derivatives **b1**, **b2** and **b3** show the lowest binding energy with oxo-Tc (-845.08, -927.58 and -970.19 kcal/mol, respectively). The binding energy of complexation of oxo-M indicates that the ligand field strengths are lower for 3^o-amine donors, **a** relative to those for 2^o-amine donors, **b**.

Acknowledgements: Financial support from the Center of Excellence for Innovation in Chemistry (PERCH-CIC), Office of the Higher Education Commission, Ministry of Education and the faculty of science, Mahasarakham University is gratefully acknowledged.

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The selective fluorescent chemosensors for Cu^{2+} ion based on BODIPY derivatives: experimental and theoretical study

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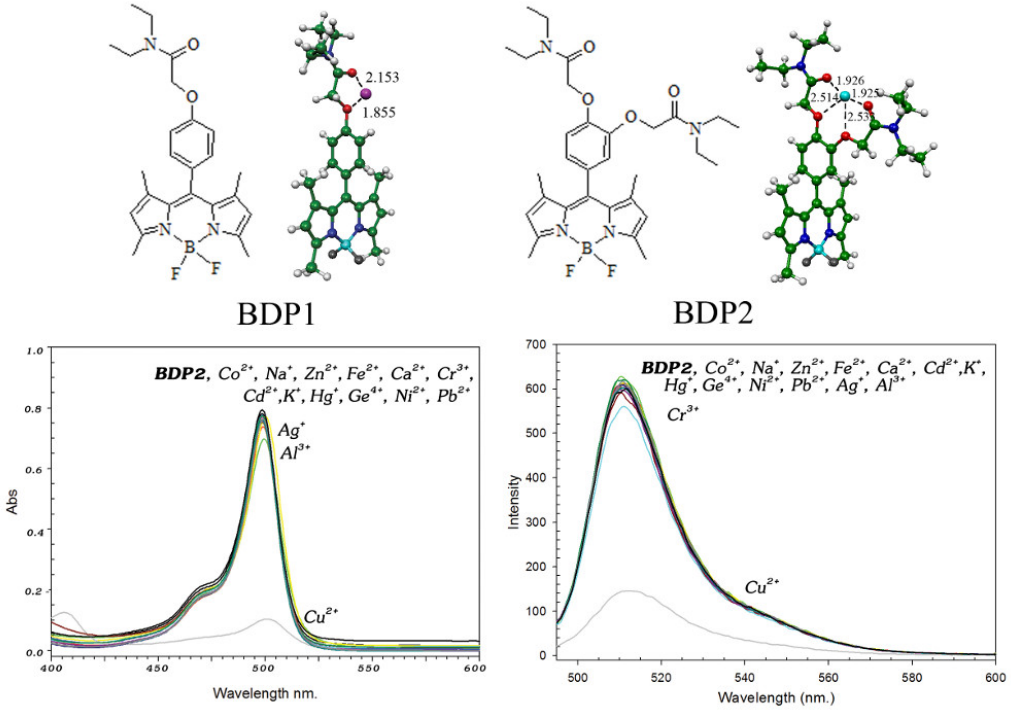
Two BODIPY derivatives for metal ion chemosensors containing 10-(4-(2-(diethylamino)-2-oxoethoxy)phenyl), **BDP1** and 10-(3,4-bis(2-(diethylamino)-2-oxoethoxy)phenyl), **BDP2** have been synthesized by coupling appropriate *N,N*-diethyl-2-(4-formylphenoxy)acetamide and 2,4-dimethylpyrrole in the presence of trifluoroacetic acid and anhydrous methylene chloride at room temperature. The excess binding abilities between these receptors and 50 equivalent of Na^{+}, K^{+}, Ca^{2+}, Pb^{2+}, Al^{3+}, Ge^{4+}, Cr^{3+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Ag^{+}, Cd^{2+} and Hg^{+} ions were studied by using UV-vis and fluorescent spectroscopy. The UV-vis and fluorescent results of **BDP2** show the most decreasing both absorption and emission intensity when Cu2+ ion was added. The complexations of BODIPY receptors with Na^{+}, K^{+}, Ca^{2+}, Pb^{2+}, Al^{3+}, Ge^{4+}, Cr^{3+}, Fe^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Ag^{+}, Cd^{2+} and Hg^{+} ions were also investigated using the density functional theory calculations at B3LYP/LanL2DZ level of theory. Calculation results point out that both **BDP1** and **BDP2** show the strongest complexation with Cu^{2+} ion. The HOMO-LUMO energy level diagrams show the excellent agreement with the optical properties.



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Molecular dynamics simulations of imidazolium-based ionic liquids - properties and structure at the interface

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Ionic liquids (IL's) are molten salts composed solely of ions, which melting point is often less than 373 K . IL's are considered to be the green solvents for industrial processes, and are seen as an alternative to the toxic organic compounds due to their characteristic properties: negligible vapor pressure and high thermal stability [1]. In the present work a molecular dynamic models of ionic liquids were established. The performance of selected force fields was evaluated as well. The microscopic structure, bulk and the interface properties were evaluated using two all-atom, non- polarizable force fields. The good agreement between simulated and experimental value as well as the temperature dependence and the cation chain-length dependence of physicochemical properties are described well. In case of dynamic properties the and reduction of short-range van der Waals interaction while leaving the Coulomb interactions unchanged allows to get reliable dynamical properties. Radial distribution functions (RDF) reveal high ordering structure of IL's and preferable conformations as well as the presence of hydrogen bonds between cations and anions and cross-linking in case of the biggest anion. All the determined properties are essential for understanding the nature of ionic liquids.

Acknowledgements: This research was financed by the National Science Center (Poland) grant no. 2011/01/B/ST/066591. Calculations were performed at the Wrocław Center for Networking and Supercomputing.

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Influence of spatial confinement on electric properties of p-Nitroaniline

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Spatial confinement influences strongly electronic structure, energy spectra and chemical reactivity of atoms and molecules, as it has been clearly demonstrated both theoretically and experimentally [1]. This is particularly true in the case of guest-host systems, of which endohedral complexes with nanotubes and fullerenes are excellent example and can serve as archetypal benchmarks. However, despite the considerable volume of data and due to extremely complicated nature of this phenomenon, our knowledge of the properties of compressed matter is still lacking.

In the present study, we have examined the electric dipole properties, namely the dipole moment (μ), polarizability (α) and first hyperpolarizability (β) of p-Nitroaniline (pNA) molecule under various approximate confining potentials. The finite-field method (FF) was applied to compute the magnitudes of relevant components of μ, α and β. The properties in question have been analyzed using a wide range of *ab initio* techniques, including Hartree-Fock approximation (HF), the second-order Møller-Plesset perturbation theory (MP2), as well as Complete Active Space Self Consistent Field (CASSCF) and Complete Active Space with Second-order Perturbation Theory (CASPT2) methods. These *ab initio* results were then used as a reference to assess the performance of selected exchange-correlation functionals employed within the Kohn-Sham formulation of density functional theory (KS-DFT).

Two model confining potentials have been considered in our study: a linear combination of Gaussian functions of spherical symmetry proposed by Benrhardsson [2] and two-dimensional, harmonic oscillator potential, mimicking a cylindrical confinement. Our results demonstrate, that the most significant influence of spatial restriction was observed for the molecular first hyperpolarizability of pNA molecule. Thus, in order to elucidate this effects, we employed a two state model to gain insight into the common factors affecting β value, that is, the transition energy, transition dipole moment and the change of polarity between ground and low-lying excited charge transfer state. Interestingly, depending on the symmetry of the applied confining potential, the predicted shifts in charge-transfer transition energies differ.

Acknowledgements: The work was financed by a statutory activity subsidy from the Polish Ministry of Science and Higher Education for the Faculty of Chemistry of Wrocław University of Technology. The computer time at the Wrocław Center for Networking and Supercomputing is gratefully acknowledged.

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Molecular dynamics simulations of multiphase systems: complementing experimental SHG studies

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The Structure of two phase glycerol/water alkane system is controversial.[1,2] Triphenyl dyes can be used to probe the interface by using Time Resolved Second Harmonic Generation spectroscopy[1] Such a system of the interface structure of glycerol/water with an alkane was simulated by Molecular Dynamics simulations. This poster presents simulation conditions and the analysis of the glycerol structure near the interface.

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Immobilization of nucleosides on quartz (101) surfaces

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An adsorption of the nucleosides on fully hydroxylated (neutral) and charged quartz(101) surfaces is studied using molecular dynamics simulations. We provide a detailed description of the binding behavior of the four nucleosides (deoxyguanosine, deoxycytidine, deoxyadenosine and deoxythymidine) on the surfaces with different surface charge densities. We analyze the best binding arrangements, and we quantify the strength of nucleosides' interactions with the inorganic surface. These results are compared with our previous results on adsorption of the pure bases. Simulated quartz surfaces cover the surface charge densities of 0.00, -0.03 and -0.06 $C.m^{-2}$, which approximately correspond to pH values 4.5, 8.5 and 9.5.

Acknowledgements: We gratefully acknowledge support from the Grant Agency of the Czech Republic P208/12/0622 and the Ministry of Education, Youth and Sports of the Czech Republic ME09062. The access to computing and storage facilities owned by parties and projects contributing to the National Grid Infrastructure MetaCentrum, provided under the program "Projects of Large Infrastructure for Research, Development, and Innovations" (LM2010005) is highly appreciated/acknowledged.

Design of low band gap copolymers for organic electronics

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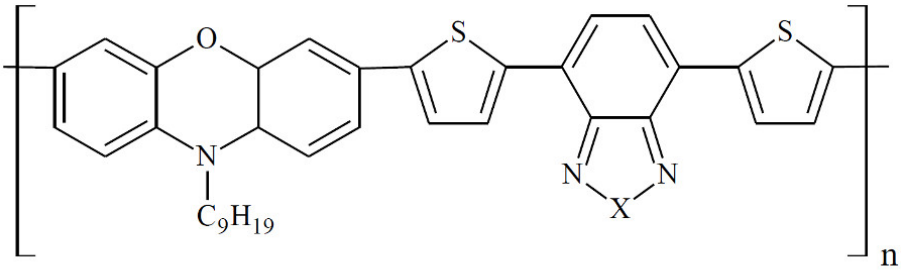
The future of organic electronics is the realization of low-cost, flexible and easy-to-process optoelectronic devices among other photovoltaic cells (OPVC, DSSC), organic light emitting diodes (OLED, PLED, WPLED), field-effect transistors (OFET) and biosensors. Attractive materials for that application are semiconducting thin films composed of low-weight molecules or polymers [1].

Optoelectrochemical properties organic semiconductors can be synthetically tuned by incorporating an electron donating and/or withdrawing unit into polymer backbone. This very useful modification allows to obtain new stable compounds with a desired energy band gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) as well as improving solubility by aliphatic chains insertion [2]. Since DFT calculations predict band gap value, it constitute reasonable tool for designed new polymer semiconductors in time and cost saving manner [3].

Theoretical investigation of new polymers based on the *N*-alkylphenoxazine, the 2,1,3-benzotiadiazol and analogical units will be presented and their potential application in organic optoelectronic devices will be discussed, Scheme 1.



X = S, N-alkil, O, Se, C, C=C

Fig. 1: Chemical structure of new *N*-nonylphenoksazine co-polymers

Acknowledgements: Authors are gratefully acknowledged Wrocław Center for Networking and Supercomputing for generous allotments of computer time.

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Peripheral and structural effects on the band gap of acceptor-donor type conducting polymers

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In this computational study, the band gap energy of an acceptor-donor type conducting polymer consisting of terthiophene repeating units with fused bisfulleroid group was estimated by extrapolating excitation energies approximated by the HOMO-LUMO energy differences as well as the TDDFT method with respect to the inverse number of monomer units. Optimizations were performed both in vacuum and in o-dichloro benzene (as solvent) using the B3LYP and MPW1B95 functionals. The calculated optical band gap was found to be in good agreement with experimentally reported band gap in the literature [1]. However, different band gaps with different experimental techniques were reported in the referred experimental study for the same system. In order to understand the reasons behind this behavior, effects of the structural (inter- and intra-molecular stacking) and environmental (explicit and implicit solvation and acidic doping) factors on the absorption of the terthiophene monomer with fused bisfulleroid were investigated. Acid-doping was found to be very important in terms of the present system.

Acknowledgements: This work was supported by İTÜ-UYBHM, grant No. 10822009.

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Theoretical study on mechanism of dehydrogenation of ammonia borane catalyzed by palladium complexes

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Ammonia Borane (NH_3BH_3, AB) is a promising material in hydrogen storage technology, mainly due to the high weight of its contents (19.4%). This is important in terms of replacement of "traditional" fuels (gasoline, oil, natural gas) by molecular hydrogen. One of the method to produce the molecular hydrogen is dehydrogenation of AB catalyzed by transition metal complexes.

In this study, based on the static DFT calculations, energy profiles of dehydrogenation reactions of NH_3BH_3 molecule, catalyzed by two complexes based on palladium, [Pd(allyl)]BF_4 and [Pd(allyl)(2,4-hexadiene)]BF_4 were determined [1]. The calculated energy profiles of dehydrogenation reactions show that the first step is the formation of η-(BH)-agostic complex of AB with the metal center. Formation of these intermediates lead to very high stabilization due to electrostatic interaction as it has been found from the combined charge and energy decomposition scheme, ETS-NOCV. Significant donation σ(BH)→Pd confirmed by ETS-NOCV, leading to elongation of B-H bonds (by ca. 0.1 Å), facilitates the first loss of molecular hydrogen solely from boron atom of AB, Fig 1.

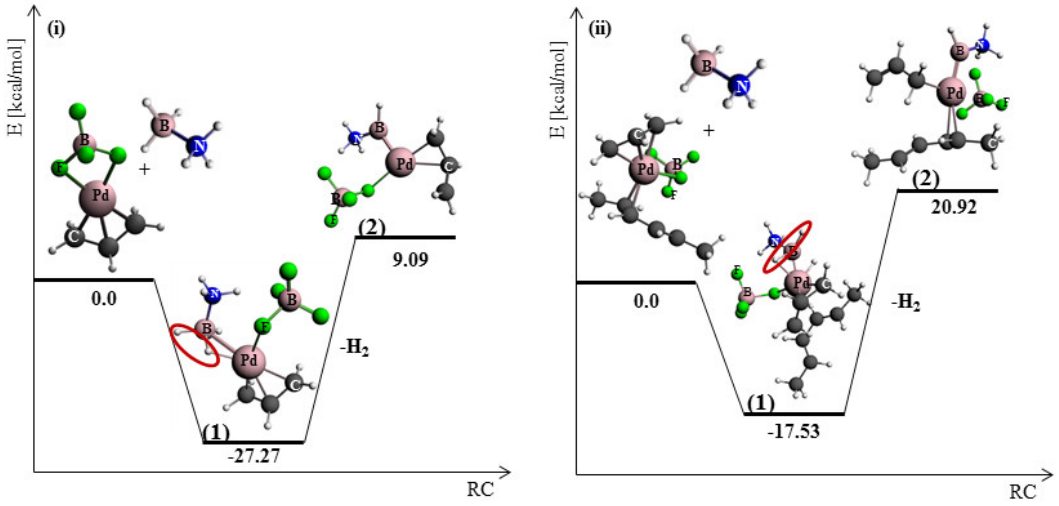

Fig. 1: Mechanism of the first dehydrogenation of ammonia Borane catalyzed by (i) [Pd(allyl)]BF_4, (ii) [Pd(allyl)(heksa-2,4-dien)]BF_4.

Activation of solely B-H bond is consistent with the experimental kinetic isotope – based findings. In addition, it was shown that allyl and 2,4-hexadiene ligands can mediate the dehydrogenation by accepting the proton from NH3 group of AB. In this work, it has also been demonstrated that the two AB molecules can simultaneously participate in the dehydrogenation when considering only [Pd(allyl)]+ model of catalyst.

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Molecular modeling as a valuable tool for the properties prediction of molecularly imprinted polymers

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Molecular imprinting is one of the widely applied method for design and manufacture intelligent materials which can recognize the target molecule specifically and selectively. Molecularly imprinted polymers (MIP) are an example of this kind of materials. The most important role in the synthetic process of MIP plays the formation of stable "template –monomer" complex in the prepolymeric system. That process determines production of cavities which are complementary to the template structure.

The molecularly imprinted polymers have a great variety of applications in analytical technology (chromatography, solid phase extraction, sensors), drug delivery systems, and organic synthesis.

Theoretical methods are very useful to choose the most suitable systems for imprinting. Moreover they are successfully used to probe polymer properties and aspects of the molecular imprinting process.

We have analyzed the energies of prepolymerization complexes of 1-(2,4-difluorophenyl)-2-(1H-1,2,4-triazol-1-yl)-1-ethanone as a template with eight various functional monomers (methacrylic acid, 2-(trifluoromethyl)-acrylic acid, acrylic acid, 4-vinylpyridine, 1-vinylimidazole, allylamine, α-methylstyrene) and with cross-linker (ethylene glycol dimethacrylate). We have used 1:4:12 (template : monomer : cross-linker) ratio. After that we have created the model of polymer cavity (double bonds in monomers and cross-linker were replaced by single bonds) which was used in selectivity studies. In our work DFT and molecular mechanics methods were applied.

Computational approach reveal the most stable conformations of each adduct formed between template, functional monomers and cross-linker, and elucidate the cavity formation. Results obtained in computational studies are in accordance with experimental data (capacity of polymers related to the template).

Molecular dynamics of ethylene polymerization processes catalyzed by half-metallocene titanium(IV) complexes

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Half-metallocene titanium(IV) complexes with aryloxo ligands attract attention of both, theoreticians and experimentalists due to their high catalytic activity in ethylene polymerization processes. Significant conformational flexibility of the catalysts causes need of considering various conformers at each reaction step. Conformational flexibility also implies existence of numerous reaction pathways and relative easiness of transitions between these pathways is observed. In this setting, molecular dynamics approach proves itself valuable and efficient.

In the present work results of molecular dynamics studies on the half-metallocene titanium(IV) catalysts are presented. Molecular systems under consideration include non-bridged half-metallocene titanium(IV) complexes with aryloxo ligand acting as catalysts in ethylene polymerization process. Catalysts with various ligands and at various catalytic process stages are considered in simulations. Wide context of the project including results of the static calculations and the experimental measurements is also mentioned.

Presented results include examples of spontaneous conformational transitions affecting catalyst activity. Moreover, spontaneous insertion of the ethylene, followed by conformational changes making the catalytic cycle in one simulation, is also shown.

Methodology of simulations includes Car-Parinello molecular dynamics on the DFT level (CPMD software package) and Born-Oppenheimer molecular dynamics on the semi-empirical level (MSINDO software package). Despite lower accuracy the semi-empirical approach is still useful due to ca. 3.5 orders of magnitude difference in computational cost comparing to the DFT approach. Free molecular dynamics is used to study spontaneous transitions (including conformational changes and ethylene insertion reactions). Constrained molecular dynamics in the slow-growth approach is used to obtain free energy profiles of the ethylene insertion reaction.

‘Extended viologens’: a quantum-chemical study

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‘Extended viologens’ (EV) are analogous to viologens, in which aryl, ethylene, or thiophene units are inserted between the pyridine units (Figure 1) [1]. Such compounds can undergo two consecutive one electron–transfer reactions to form a stable radical cation in the first step and then a neutral state in the second. The latter state can exist in different spin multiplicities. This rich electrochemical behavior of EV gives rise to an interesting combination of electronic, optical, and magnetic properties. Therefore, they are regarded as very promising materials with potential applications in electrochromic devices and field-effect transistors. In addition to the purely applied aspect, the description of the structure and properties of EV and especially of their biradical singlet states represents a challenge from the theoretical point of view.

The present work is focused on quantum-chemical calculations of EV, represented in Figure 1. The geometry optimizations and the vibrational frequency analyses have been performed for all forms in vacuum as well as in tetrahydrofuran and acetonitrile within the PCM scheme together with the modified LC-BLYP exchange-correlation functional (μ= 0.33) and the 6-31+G* basis set. The UV-*vis* spectra have been simulated using time-dependent density functional theory and multi-reference approaches and the results have been interpreted from the standpoint of the available experimental data.

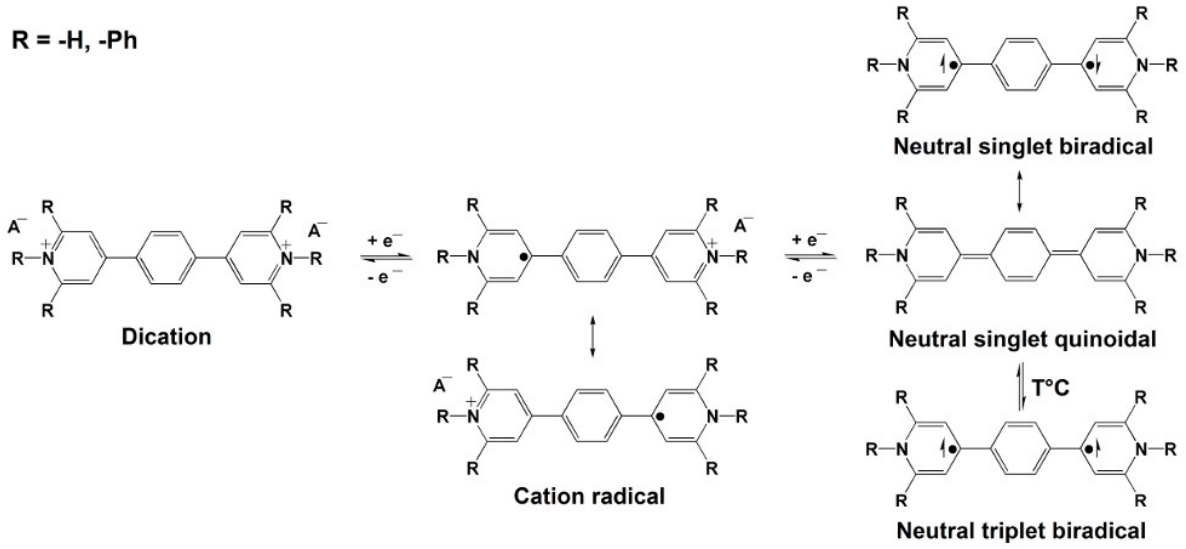

Fig. 1: ‘Extended viologens’ investigated in the present work.

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Aromatic organo-beryllium compounds – effect of substituent on hydrogen adsorption properties

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Beryllium dimmer (Be_2) can act as a sp^2 carbon atom in aromatic hydrocarbon compounds (e.g. benzene, naphthalene) [1]. This organometallic compound can adsorb one hydrogen molecule per Be2 moiety with the adsorption energy in the range of 5-6 kcal/mol. Hydrogen storage properties of this moieties can be further enhanced by changing the hydrogen atom by substituent groups. The proper substituent in aromatic organoberyllium compounds can increase the hydrogen adsorption energy up to 8 kcal/mol. Moreover it allows to adsorb second H_2 molecule per Be_2 center with the energy up to 6 kcal/mol. The substituent effect on molecular hydrogen adsorption properties of aromatic organo-beryllium compounds is presented in this work. Structures and hydrogen adsorption properties of these compounds were calculated applying the MP2 approach.

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Catalytic methane aromatization on MoO_3/ZSM-5: theoretical studies on reaction mechanism

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The rapid development of industry and global economy resulted in an increased need for energy. It is thus essential to seek new energy sources and ways of their effective usage. The proven world natural gas resources have already overcome those of oil, and as such, the natural gas emerges as a promising substrate for synthetic fuel production. The main drawback of using natural gas is that ca. 40% of it is located in remote areas making it difficult or even impossible to transport through pipelines. Consequently, the focus is to transform it into transportable liquids on-site. There are several ways to transform natural gas into fuels and valuable chemicals, one of them being aromatization. One of the systems used for CH_4 aromatization is based on MoO_3/ZSM-5.

The aim of the present studies is to model 1) the possible intermediate structures through which the precursor of the active phase, i.e. MoO_3, is transformed to give molybdenum (oxo)-carbides and 2) the catalytic reaction in which methane is activated and converted to ethylene. The reported studies are preformed within Density Functional Theory (DFT) method in both cluster and periodic approaches.

The thermodynamic considerations reveal that the reduction of molybdenum trioxide by methane is endoenergetic. Upon a process, a formation of C_2 and CO is observed, in agreement with experimental data. Methane is activated on the reduced form of the catalyst. The resulting CH_3 and H radicals are bound to the reduced Mo center. Next, the second hydrogen atom from CH_3 group is abstracted. The resulting H_2 molecule desorbs from the catalyst. Ethylene might be then formed as a result of recombination of two CH_2 groups present on the adjacent molybdenum centers.

Acknowledgements: This work was supported by the project EC 7th FP NEXT-GTL „Innovative catalytic technologies & materials for next gas to liquid processes".

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Charge transfer in systems Fe-SWCNT and Fe-graphene

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Metal-intercalated single-wall nanotubes and graphene monolayers are perspective materials for nanoelectronics. Up to now, only calculations for nanotubes with alkali metal inside have been performed [1–3]. For graphene there is some investigation of gold- and lithium-intercalated systems, mostly in case of decoupling of grapheme layer from the substrate [4,5]. We have now performed computational simulations of systems, in which iron atom intercalated in single-wall carbon nanotubes (SWCNT) or attached to surface of grapheme particles. All calculations were done using the VAMP program package [6], employing the UHF AM1* method. Both metallic (4.4) and semiconducting (7.0) nanotubes were investigated.

The results of our calculations show that there is a charge transfer between the iron atom and the sp2-hybridixed carbon surface. The conjugated system can donate or accept electrons from the iron atom depending on the charge of the whole system. Irrespective of the charge of the whole system (taking into account the possible oxidation states of the iron atom, the charges 0, +1, +2, +3 were considered) the charge of the iron atom was in the range of +0.88e ... +1.08e.

The charge of the iron atom depends on its position in the nanotube or on a grapheme layer. Most stable configuration of a system usually corresponds to hapticity=2 and position of an atom/ion over center of a bond.

No substantial charge delocalization was found. The negative charge is mainly localized on the two carbon atoms, which are close to the metal ion. The calculations performed for H-terminated allotropes showed that the carbon part of the system charged negatively, even when the charge of the whole system reached +3 (charge of whole system +2). Thus, there is a charge transfer from the hydrogen atoms to the carbon part of the system.

Potential barrier of movement of an atom was found to be smaller than 10 kcal/mol.

Investigations with other metals, nanotubes of other diameters and other terminated atoms are in the process.

Acknowledgements: This work was supported by the Deutsche Forschungsgemeinschaft as part of SFB953 "Synthetische Kohlenstoffallotrope" and by a grant of computer time on the Höchstleistungsrechner in Bayern II (HLRB II).

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Physical origins of 2,2′-bithiophene dimer stability. A DFT-SAPT study

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Poly-3-alkylthiophenes are one of the most popular polymers used in organic electronics [1]. High charge carrier mobility (in polymorphous layer $\mu = 10^{-3}$ cm^2/Vs) and good solubility (polymer layers can be deposited with commonly used wet techniques such as spin-coating, ink-jet printing or spraying) make these polymers one of the most widely used as hole transporting layer in organic field effect transistors, luminescent diodes and photovoltaic devices [2]. Their good conducting properties arise from the conjugated π-bond system and ordered lamellar structures created in the polymer layers and solutions.

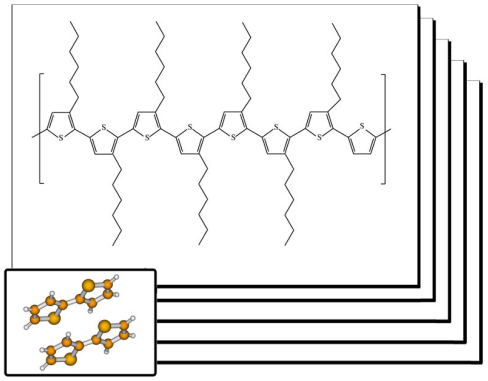

Fig. 1: Poly-3-alkylthiophene layer structure and theoretical model of 2,2′-bithiophene dimer.

In the present work, the stability of 2,2′-bithiophene dimer is investigated. We consider this dimer to be a simple model describing intermolecular interactions in polyalkylthiophene layer. Supermolecular approach and the SCS-MP2 method are used to obtain the interaction energy hypersurface IEH (spanned by four configuration parameters: rotational angle and intermolecular separations in three dimensions).
For selected intersections of IEH, further analysis of the influence of individual types of interactions on the stability of the system is performed. In doing so, two energy decomposition approaches are compared: the hybrid variational-perturbational scheme based on the MP2 method and the DFT-SAPT approach [3, 4].

The suitability of these methods in describing the stacking π-π dispersion interactions is also discussed. In particular, we focus on the approaches to determine the dispersion interactions. The results based on above mentioned analysis should provide a solid basis for force-field parametrization for molecular dynamics simulations of polyalkylthiophene layers which, on the other hand, are expected to provide reliable structures for charge transport calculations.

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Theoretical study of carbon dioxide hydrogenation: reaction thermodynamics and potential intermediate products

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One of the promising methods for carbon dioxide utilization is hydrogenation into hydrocarbons, which could be used, i.a., as fuel components. This solution can be treated as CO_2 recycling and could be used for production of fuels with simultaneous decreasing of CO_2 emission and saving of fossil resources [1, 2].

Design of a suitable catalyst for this process requires comprehensive analysis of potential reaction mechanisms and intermediate products with prediction of thermodynamics [3]. In this study, reaction mechanism was proposed and investigated on active center with intra-framework titanium.

A fragment of MFI zeolite framework was used for models construction, where intra-framework Ti atom was introduced.

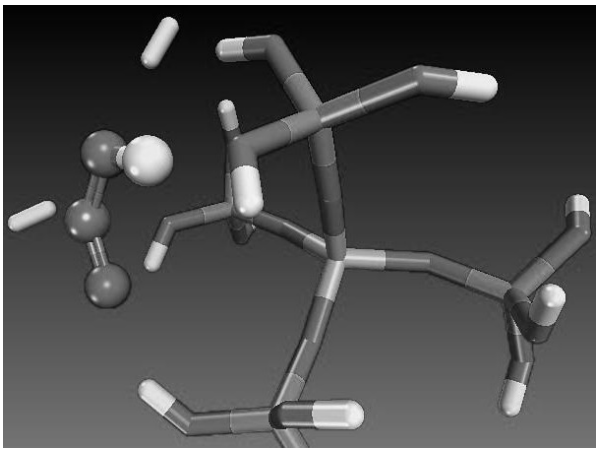

Fig. 1: Intermediate product.

Presented work is focused on studying potential reaction path, intermediate products and calculation of reaction thermodynamics.

The scope of the work includes construction of clusters, optimization of structures corresponding to intermediate products and thermodynamics calculations. Calculations were performed using DFT method (Accelrys Materials Studio DMol3 [4]) with DNP basis set and PBE functional.

We have found, that reaction goes over three intermediate stages, one of them (fig. 1) is worth particular interest, because of its high energy and it might probably correspond to transition state. Formation of this intermediate seems to be the limiting stage of the reaction, as its energy barrier equals 3,94 eV.

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Algorithm for generating random host-guest configurations: implementation as Zeobuilder module and examples of potential applications

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Indicating most preferable adsorption sites in porous materials requires analysis of large number of configurations between host structure and guest molecule. In other words, it is necessary to generate multiple locations of guest molecule in porous structure and calculate energy of each system, relatively, optimize geometry.

Available codes designed for this purpose, like Adsorption Locator [1] from Accelrys Materials Studio software package [2], are based on calculations with force fields. However, there is no software for docking simulations using DFT method. Presented here code allows to directly perform docking simulations with DFT based calculations.

The algorithm was implemented as a module for Zeobuilder [3]. The procedure imports a model, that includes both host and guest structure and generates user defined number of configurations, where guest molecule is in randomized location. Configurations, where distances between host and guest atoms are shorter than minimal contact (user customized parameter) are rejected to avoid models where two atoms are too close to each other. Accepted structures are converted into input file (single point energy calculation or geometry optimization) for SIESTA [4] and can be directly submitted.

Acknowledgements: Calculations were performed at the Wrocław Center for Networking and Supercomputing and at Interdisciplinary Center for Mathematical and Computational Modeling.

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Solvent effect on the vibrational spectrum of Michler's ketone: an experimental and theoretical investigations

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Michler's ketone is an aromatic amino ketone, benzophenones derivative, used as an intermediate product in the manufacture of triarylmethane dyes and also as a sensitizer. Its solvatochromic properties were widely studied because it appears to be a suitable tool for investigating liquids and solid environments polarity. In an attempt to further analyze differences and correlations between experimental results obtained by using other spectroscopic methods and compare them with each other, we have studied IR spectra of Michler's ketone. We consider the IR spectra for the intermolecular interaction properties of Michler's ketone dissolved in carbon tetrachloride, cyclohexane, chloroform, 2-butanone, acetone, DMSO, acetonitrile and methanol solvents, focusing on solvent effect. It has been found that change of empirical solvent polarity parameter has ambiguous influence on absorption bands transitions and bond lengths.

Experimental investigations have been supported by the quantum-mechanical computations to gain more insight into the solvatochromic behavior of Michler's ketone. Calculations have been carried using Kohn-Sham formulation of Density Functional Theory and the Polarizable Continuum Model was employed to account for solute-solvent interactions.

Structural and spectroscopic characterization of model carbon nanotubes

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Single wall carbon nanotubes and their derivatives are very interesting targets for both basic science and industry. Selected simple models of carboxylated zigzag (4,0) single wall carbon nanotubes (SWCNT-COOH, see Fig. 1) and hydroxylated systems [1, 2] were fully optimized using Gaussian09 program [3], "standard" hybrid density functional B3LYP and several basis sets. We investigated a convergence of electronic, geometric and spectroscopic properties of tip-functionalized model SWCNT systems with hydroxyl and carboxylic groups upon increasing the model size. The analysis of converging parameters with the size of the system was based on our earlier work dealing with estimation of NMR parameters in the complete basis set limit [4, 5].

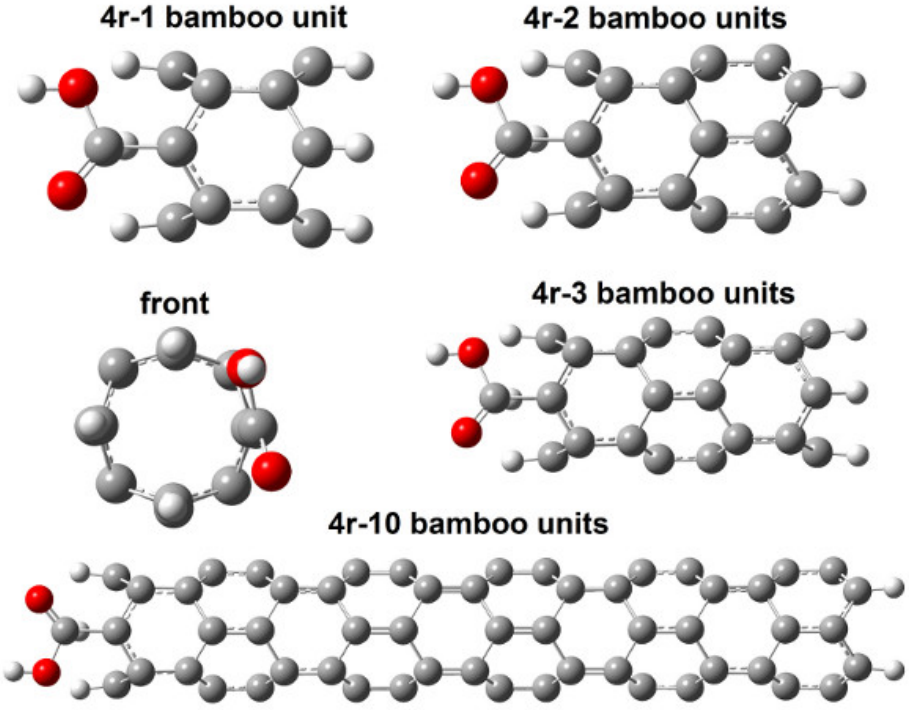

Fig. 1: Carboxylated cyclacene and model zigzag (4,0) single wall carbon nanotubes .

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DFT-D method designed for graphitic systems

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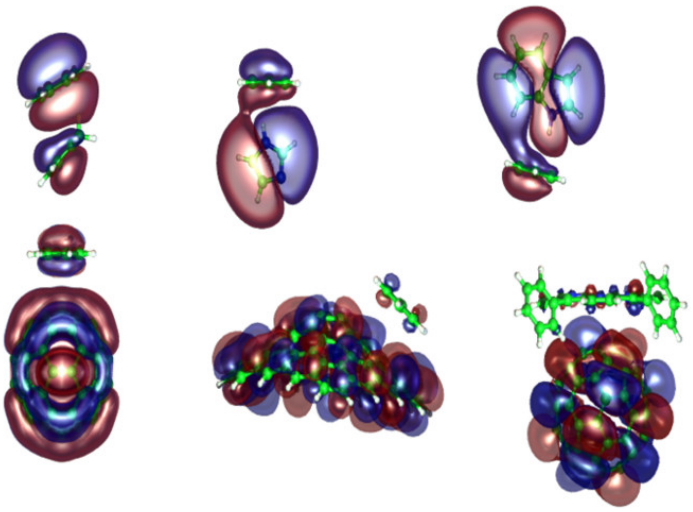
Noncovalent interactions plays important role in graphitic materials, but they are very hard to model from theoretical point of view. Precise ab initio methods (e.g. coupled cluster methods) are not feasible for such large systems and other methods, like MP2, are usually not accurate enough.

Density Functional Theory (DFT) methods are feasible, but lack proper dispersion. Grimme proposed augmentation of DFT method with empirical dispersion correction, so called DFT-D method. It was proven to accurately describe Van der Waals (VdW) interactions [1–3]. New DFT-D parameters, designed especially for graphitic materials were obtained using, very accurate, CCSD(T) data on benzene dimer as a reference [4].

Binding energies for various graphitic-type systems are presented. From small structures, as protonated benzene dimer, to large complexes, like C_{60}-tetraphenylporphyrin. Obtained binding energies are consistent to literature data, which shows that new DFT-D parameters, although obtained using benzene dimer are transferable to all graphitic materials.



Acknowledgements: This work was supported by the Portuguese *Fundação para a Ciência e Tecnologia* through the Doctoral Program on Sustainable Chemistry, grant no. SFRH/BD/61894/2009, the project SeARCH (CONC-REEQ/443/2005)

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Density functional theory considerations on the push-pull D-π-A anions possessing double or triple bonds

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Nowadays, the Kohn-Sham formulation of density functional theory (DFT) is one of the tools, that are most commonly used in quantum chemistry calculations. However, in many instances the effectiveness and accuracy of DFT method is still not fully evaluated. Thus there is a strong necessity to investigate the performance of various DFT exchange-correlation functionals.

In our study we are elucidating the effectiveness of selected DFT functionals in prediction of one-photon absorption spectra of two p-nitrophenolates molecular systems with alkene and alkyne spacers. Recently Kirketerp et al. [1] have published the experimental state-of-the art spectra for this compounds measured in the gas phase. They concluded that change in bond ordering from double to triple causes the red shift of absorption maximum by 10nm. This work [1] provides an unique opportunity of direct comparison between experimental and theoretical results.

In our investigations most of the employed DFT functionals, regardless of the basis set used, are reproducing the red shift connected with bond ordering. However, comparing with the experimental data, the calculated vertical excitation energies are mismatched.

Acknowledgements: This work was supported by a statutory activity subsidy from the Polish Ministry of Science and Higher Education for the Faculty of Chemistry of Wrocław University of Technology. Calculations were performed at the Wrocław Center for Networking and Supercomputing.

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DFT theoretical study of interactions between Ag_n (n=1-7) clusters and alpha-quartz (001) surface

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The properties of metal island films (MIFs), in particular, connected with their specific optical behavior are widely used in the last decade to produce the high performance selective absorbers, optical polarizers, and data storages, etc. The unique optical behavior of MIFs opens new perspectives for production of non-expensive photonic heterostructures. For the progress in this area it is very important to understand the details of interactions between metals that form MIFs and substrate they sputtered on.

In the present study, the first-principle calculations have been applied to investigate an electronic structure and adsorption energy of silver clusters Ag_n (n=1-7) deposited on the alpha-quartz (001) surface and analysis of minimal energy paths for diffusion of silver in alpha-quartz. The structures of most stable silver clusters on SiO_2 surface have been optimized and correlations between the cluster size and its adsorption energy have been analyzed.

All calculations have been performed with the CP2K code [1] and Firefly package [2]. The technique based on the Quickstep [3] implementation of the density functional theory (DFT) method with Gaussian and plane waves (GPW [4]) scheme has been utilized. We have used the generalized gradient functional PBE and the Goedecker-Teter-Hutter [5] pseudopotentials in conjunction with DZVP basis sets.

Acknowledgements: We thank the Research Computing Center of Lomonosov Moscow State University for the facilities and the use of the SKIF MSU "Chebyshev" and "Lomonosov" Supercomputer. This work was partially supported by the RFBR grant No 11-03-00040a.

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Structures and vibrational spectra of 1:1 and 1:2 complexes between 2-(2'-Pyridyl)benzimidazole and its 1-methyl derivative and water molecules

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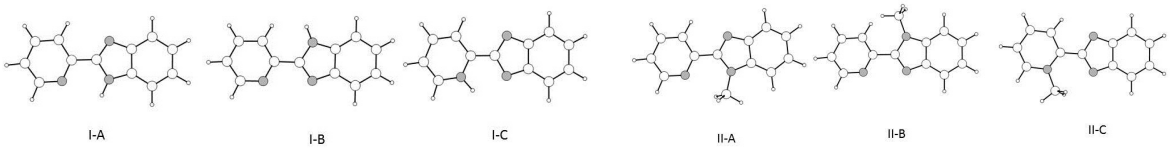
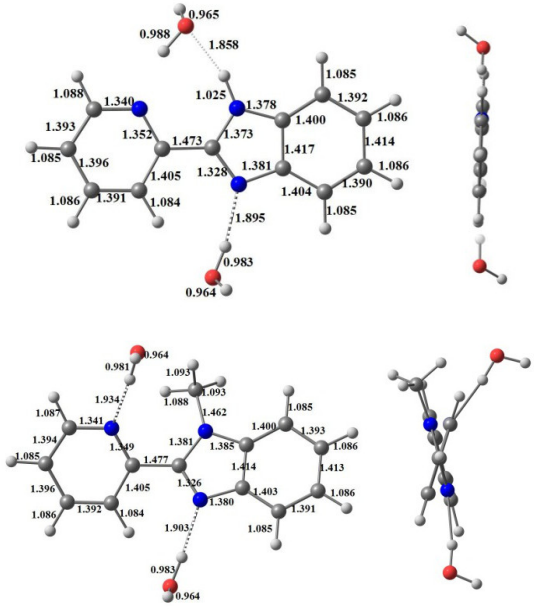
2-(2'-Pyridyl)benzimidazole (2PBI, I) and 1-methyl 2-(2'-Pyridyl)benzimidazole (M2PBI, II) can exist in three different structures:



2PBI M2PBI

Two of them (A and B) can be considered as rotamers while form C is a tautomer. Earlier it was established that the I-C form is the least stable one [1]. In this work the structures and molecular spectra of three possible conformations of M2PBI and 1:1 and 1:2 complexes of 2PBI and M2PBI and H_2O molecules have been investigated within DFT theory at the B3LYP/6-31+G** level. DFT calculations were performed with program GAUSSIAN 03 (Revision C.02) package [2]. The minima of the potential surface were found by relaxing the geometric parameters with the standard optimization methods. Analytical force constants were derived and harmonic vibrational frequencies were calculated at all investigated theoretical levels. As examples two of optimized configurations of 2PBI-2H_2O and M2PBI-2H_2O complexes are presented in Figure below. Additionally, similar calculations of some C_3H_7- and C_6H_13-substituted 2PBI ligands have been carried out. Based on DFT calculations the relative stabilities, theoretical structures, vibrational spectra and molecular force fields of considered 2PBI and M2PBI complexes have been analyzed and compared to experimental data when appropriate. Our results allow us to generalize the conclusions on analytical and characteristic frequency regions and molecular force fields behavior of 2PBI containing ligands with conformational flexibility.



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Computational investigation of the absorption of carbon dioxide into alkanolamine solutions

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Aqueous solutions of alkanolamines are the chemical absorbents that have been used extensively for the CO_2 capture from a gas stream. In this work, quantum chemical analyses were applied to investigate the CO_2 absorption reactions

$$2R^1R^2NH + CO_2 \longrightarrow R^1R^2NCOO^- + R^1R^2NH_2^- \quad (1)$$

$$R^1R^2NH + CO_2 + H_2O \longrightarrow HCO_3^- + R^1R^2NH_2^- \quad (1)$$

where R^1 and R^2 represent the alkyl group $(CH_2)_mCH_3$ and the alcohol group $(CH_2)_nOH$, respectively. We focused on the product ratio between carbamate and bicarbonate, $[R^1R^2NCOO^-]/[HCO_3^-]$, which is one of the important factors for determining the performance of CO_2 absorbents, and examined the dependence of alkanolamine structures on the absorption reactions by varying the alkyl chain length ($m = 0 - 4$) and the alcohol chain length ($n = 1 - 5$).

To predict the product ratio from the Gibbs free energies of reaction (1) and (2), we applied the conductor-like screening model for real solvents (COSMO-RS) method coupled with the density functional theory (DFT) [1]. We also performed transition state optimizations and intrinsic reaction coordinate calculations in the aqueous phase by DFT with the latest continuum solvation model (SMD/IEF-PCM) [2]. The effect of conformational variations should be also considered especially for reactions in the solution phase. For this purpose, locally stable conformations were determined using molecular mechanics.

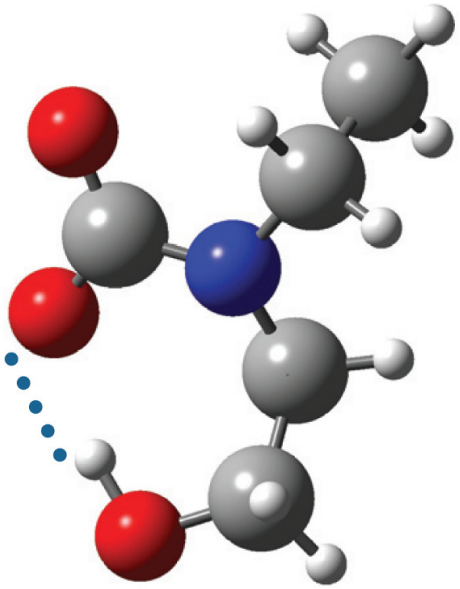

Fig. 1: Intramolecular hydrogen bond.

The calculation results predicted that the product ratio was strongly affected by the length of alcohol chain, while it did not differ significantly by varying the alkyl chain length. This prediction was confirmed experimentally by observing quantitative ^{13}C nuclear magnetic resonance spectra. In the range of alcohol chain lengths investigated in this work, the effect of alcohol chain length on the product ratio can be attributed to the hydrogen bond effects, indicating that neutral alkanolamine, protonated alkanolamine and carbamate anion are likely to form ring structures by the intramolecular hydrogen bonds of $NH\cdots HO$, $NH_2^+\cdots OH$ and $NCOO^-\cdots HO$ (Figure 1), respectively. The observed sensitivity to the alcohol chain length implies that these intramolecular hydrogen bonds play important roles in the actual absorption reactions.

Acknowledgements: This work was financially supported by the COURSE 50 project funded by the New Energy and Industrial Technology Development Organization, Japan.

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A computational model for selectivity evaluation of molecularly imprinted polymers

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A computational model was proposed to evaluate the affinity and selectivity of 2-(3,4--dimethoxyphenyl)ethylamine (homoveratrylamine) imprinted polymers. Four functional monomers: methacrylic acid, 1-vinylimidazole, 4-vinylpyridine, and allylamine were taken into account. Affinity is described as the amount of the template molecule adsorbed on MIP as compared with NIP, and selectivity is described by a comparison of adsorption of the selected compounds on MIP. The most promising monomer was chosen on the basis of the energies of prepolymerization complexes. The structure of the most stable complex was used to simulate the cavity in the polymer matrix, which was then used in selectivity studies. In the computations, solvent effects were approximated by the distance dependent dielectric constants εr_{ij}. Theoretical results were compared with the experimental values of the imprinting factors (IF) for homoveratrylamine, and to the bound amounts of selected catecholamines and other biogenic compounds. It was showed that polymer created from monomer which forms the most stable prepolymerization complex shows the highest selectivity towards homoveratrylamine. The binding energy between cavity and the analyte was in agreement with the experimental binding capacity.

The proposed computational procedure can be used for successful evaluation of the imprinted polymers.

Determination of Platinum(IV) reduction potential

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Platinum complexes are one of the most used and efficient complexes concerning tumor treating. In this study we are focusing on Pt(IV) complexes of satraplatin (JM216), tetraplatin (NSC-63812) and JM149 and corresponding reduced forms of Pt(II).

In the study, quantum chemical methods were employed. All the structures were optimized using the ωB97XD/6-31+G* level of calculations with corresponding Stuttgart pseudo-orbital (and pseudopotencials) on Pt and Cl atoms. Liquid environment was simulated by IEF-PCM with UFF cavities. The SP analyses of optimized complexes were performed using 6-311++G(2df,2pd) basis employing several levels of computation: MP2, CCSD and DFT (B3LYP, ωB97XD). Water solution simulated by DPCM implicit solvent with scaled-UAKS cavities (as mentioned in ref. [1]) was used.

For all the complexes, decomposition energy analysis (bonding energies) were determined, NBO partial charges were compared at all selected levels, and AIM bond critical points examined. Also, averaged local ionization potential (ALIP) and molecular electrostatic potential (MEP) were explored. For all Pt(IV) complexes reduction potential evaluated.

Acknowledgements: Support from Grant Agency of Czech Republic No. P205/10/0228 is acknowledged. The access to the META Center supercomputing facilities is acknowledged.

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Testing the applicability of the differential transition state stabilization approach and atomic multipole expansion in the design of new biocatalysts

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Recent successes in theoretical design of theozymes with new catalytic functions [1] indicate also some deficiencies in currently applied methodology and the need to develop more effective biocatalyst design techniques [1, 2].

In one of such theoretically designed enzymes PT3 eight mutations in adenosine deaminase resulted in obtaining very moderate activity towards diethyl-7-hydroxycoumaryinyl phosphate (DCEP) hydrolysis [1]. However, much more active version PT3.3 was discovered later by directed evolution experiment [1], where additional mutations of residues 57, 58, 59, 62, 186, 218 and 299 were included in the second coordination sphere.

As the above mentioned mutations were not predicted theoretically [1] our goal is to analyze whether these mutations could have been predicted by the more complete theoretical model taking into account differential transition state stabilization [3] and higher atomic multipole moments [4].

Acknowledgements: The research was supported by Wrocław Research Center EIT+ under the project "Biotechnologies and advanced medical technologies-BioMed" POIG.01.01.02-02-003/08 financed from the European Regional Development Fund (Operational Program Innovative Economy, 1.1.2). Calculations were performed at Wrocław Center for Networking and Supercomputing.

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Molecular mechanisms of DNA point mutations induced by the deamination of adenine: comprehensive quantum-chemical study

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The molecular structures, relative stability order and dipole moments of a complete family of 21 planar hypoxanthine (Hyp) prototropic molecular–zwitterionic tautomers including ylidic forms were computationally investigated at the MP2/6-311++G(2df,pd)//B3LYP/6-311++G(d,p) level of theory in vacuum and in three different surrounding environments: continuum with a low dielectric constant (ε=4) corresponding to a hydrophobic interface of protein-nucleic acid interactions, dimethylsulfoxide (DMSO) and water.

We found out that neither intramolecular tautomerization by single proton transfer in the Hyp base, nor intermolecular tautomerization by double proton transfer in the most energetically favorable Hyp·Hyp homodimer (symmetry C_{2h}), stabilized by two equivalent N1H...O6 H-bonds, induce the formation of the enol tautomer (marked with an asterisk) of Hyp with *cis*-oriented O6H hydroxyl group relative to neighboring N1C6 bond. We first discovered a new scenario of the keto-enol tautomerization of Hyp·Hyp homodimer.

We first showed that Hyp*·Thy mispair (C_s) converts to the wobble Hyp·Thy base pair (C_s) *via* high- and low-energy transition states and intermediate Hyp·Thy*. The authors expressed and substantiated the hypothesis, that the keto tautomer of Hyp is a mutagenic compound, while enol tautomer Hyp* does not possess mutagenic properties. The lifetime of the nonmutagenic tautomer Hyp* exceeds by many orders the time needed to complete a round of DNA replication in the cell.

For the first time purine-purine planar H-bonded mispairs containing Hyp in the *anti*-orientation with respect to the sugar moiety – Hyp·Ade_{syn}, Hyp·Gua^*_{syn} and Hyp·Gua_{syn}, that closely resembles the geometry of the Watson-Crick base pairs, have been suggested as the source of transversions.

An influence of the surrounding environment (ε=4) on the stability of studied complexes and corresponding transition states was estimated by means of the conductor-like polarizable continuum model (CPCM).

Acknowledgements: This work was partly supported by the State Fund for Fundamental Research of Ukraine within the Ukrainian-Russian (0111U006629) and Ukrainian-Slovenian (0111U007526) research bilateral projects.

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The strength of hydrogen bonds between water and model dehydropeptides

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The structures and functions of biological molecules are primarily determined by hydrogen bonds. For example, the secondary structures, α-helices and β-sheets of protein, are stabilized by N-H···O hydrogen bonds between neighboring amino acids in the primary amino acid sequence of the protein.

The biological selectivity of a peptide greatly depend on their conformational properties. To overcome the problem of low selectivity, some modifications of model peptide structure were performed. One of them is the introduction of a conformationally rigid α,β-dehydroaminoacid residue [1, 2]. This modification leads to changes of the conformational properties of the peptide. Besides, it could have an additional impact on the strength of the intermolecular H-bond.

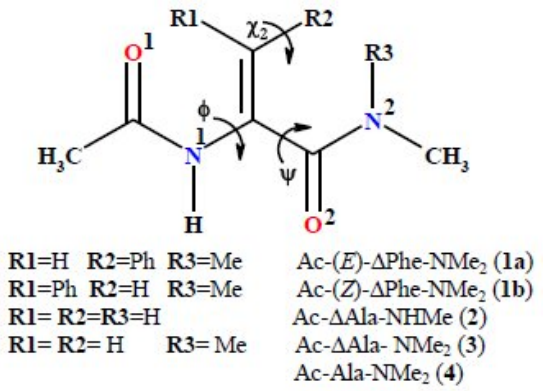

Fig. 1: General formula for the studied compounds.

Thus, the proposed chemical modification of the main structure could have a significant influence on the interaction with environment, including solvent. From IR spectra of dehydroalanine residue in polar solvents in comparison to standard analog, a higher tendency of association in the former system is evident [1]. Unfortunately, the origin of this behavior is not fully understood yet.

In order to get a deeper insight to this problem, the detailed theoretical studies were conducted. Several model diamides were selected (Fig.1). Theoretical calculation at MP2, B3LYP, M06 levels of theory, and using 6-311++G(d,p) basis sets were performed for nine low energy diamide - water complexes. The obtained results indicate that the extended conformations of all the studied models form significantly weaker hydrogen bond with a water molecule then other conformations of these compounds. The strongest intermolecular H-bond with water (Fig. 2) was predicted for diamide Ac-(Z)-ΔPhe-NMe2 (1b) in helical A conformation and open structure H.

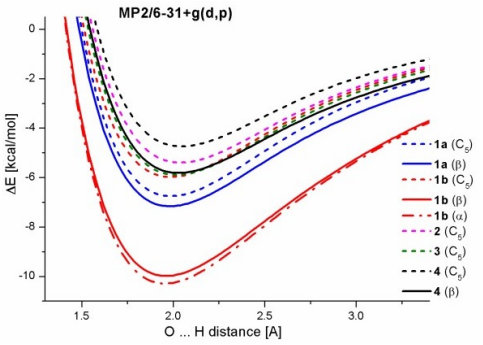

Fig. 2: Comparison of diamide-water system energy with the intermolecular bond distance, between the NH proton and the water O acceptor.

Acknowledgements: A.B. is recipient of a PhD fellowship from a project funded by the European Social Fund. Calculations were carried out in Wrocław Center for Networking and Supercomputing and in the Academic Computer Center CYFRONET, AGH, Kraków.

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Interaction between lignin and vegetable oil transesterification catalysts: A DFT study.

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Lignin is the second most abundant natural polymeric material on Earth. All vegetable materials have a large amount of this polymer (about 25% in mass on the vegetable biomass [1]). Together with cellulose and hemicellulose, it represents one of the main macromolecules in the plant-based biomass. Currently, several studies are being developed to exploit lignin as a secondary source of energy via its conversion to ethanol [2]. Other studies have reported the ability of some natural polymeric material as catalyst for vegetable oil transesterification [3] – the main way to produce biodiesel. This ability is based on the possibility to turn a homogeneous catalytic process into a heterogeneous one through the doping of the natural polymer with widely-used homogeneous catalysts.

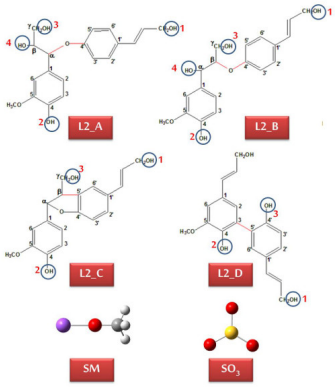

Fig.1 Structures studied in this work. The binding sites evaluated are marked as 1-4.

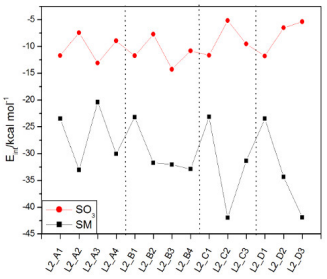

Fig.2 Interaction energy profile for SM and SO_3 with lignin models (gas phase).

In the present work we have carried out a theoretical study to understand the interaction between lignin models and the two most commonly used homogeneous catalysts in the transesterification of vegetable oils: Sulfur trioxide (SO_3) and Sodium methoxide (SM) [4] – Figure 1. The calculations were carried out using density functional calculations as implemented in Gaussian 03 software [5]. Both gas phase and, continuum based, solution (PCM/UAHF model – $\varepsilon = 32.6$) calculations were performed.

All the geometries were optimized at the B3LYP/6-31G level of theory. The interaction energies have been calculated applying the BSSE correction (B3LYP/6-31+G*//6-31G). Our results support a special selectivity for each binding site, depending on the catalyst agent used (Figure 2).

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Non-empirical quantum chemical studies of carboplatin biotransformation

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Carboplatin is a second generation Pt-based drug, selected from cisplatin derivatives of reduced toxicity. Its low toxicity is attributed to slower hydrolysis of kinetically less labile carboxylate as compared to chloride anions of cisplatin. The mechanistic aspects of aquation have been widely investigated at cisplatin, while the carboplatin activation remains still uncertain [1].

In this work we continue the in silico studies on mechanism of aquation of Pt-based drugs [2]. This step is crucial for pathways diverging towards attack on DNA or on other biological molecules. We have used two mode of reaction substrates: (1) carboplatin + H_2O, and (2) carboplatin + (eH_2O)-. Simulating two competing mechanisms it is aimed to find the nonempirical evidences for a real pathway of carboplatin biotransformation.

Applying quantum chemical calculations based on supermolecular approach, the reactions mimicking presumed steps of carboplatin activation were evaluated. The electronic structure of model systems was studied using density functional (DFT) within the newest Burda et al. adjusted basis set and GAUSSIAN-09 package [3]. The respective energy was evaluated with the use of B3LYP density hybrid functional. The calculation was performed for gas phase and water solution and the solvent effects were studied by using the polarizable continuum model.

Acknowledgements: The numerical calculations have been performed mainly at the Wrocław Center for Networking and Supercomputing.

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8-Bromo-2'-deoxyguanosine-3',5'-diphosphate – from electron attachment to the O-P bond cleavage

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Low energy electrons (LEE) are generated in a large amount during water radiolysis. Even if their genotoxic characteristics, i.e. the capability of producing single (SSBs) and double (DSBs) strand breaks in native DNA, are still disputable, their impact on DNA modified with the halogen derivatives of nucleobases (Hal-NBs) is widely approved. Thus, Hal-NBs may, in principle, be used as radiosensitizers in future cancer radiotherapy.

Studies carried out on halouracils proved that 5-bromouracil (BrU) is the most sensitive towards LEE impact. This suggests that the bromoderivatives of nucleobases should be tested against their radiosensitizing properties. In addition, the results of our recent B3LYP computational study suggest that, if incorporated into DNA, 8-bromoadenine (BrA), 5-bromocytosine (BrC) and 8-bromoguanine (BrG) should sensitize the biopolymer to electron-induced damage as efficiently as BrU does.

To partially fill the gap in the knowledge related to the radiosensitizing properties of bromonucleotides, in the current project we examine the mechanism of the electron-induced debromination of 8-bromo-2'-deoxyguanosine-3',5'-diphosphate (8BrdGDP) followed by subsequent radical reactions that ultimately lead to the O-P bond break – a model of SSBs formation in DNA (see Figure 1).

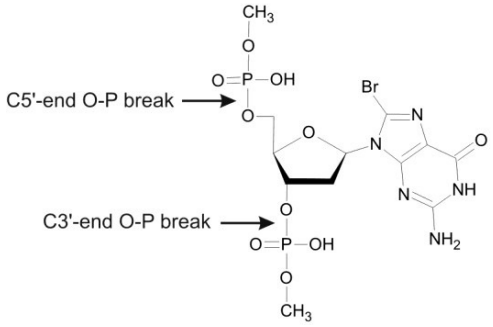

Fig. 1: Scheme of 8BrdGDP. Arrows pointed at bonds expected to be broken.

We have applied the density functional theory method with the Becke's three-parameter hybrid functional (B3LYP) and the 6-31++G** basis set. Both, the gas phase and aqueous solution (PCM model) models have been considered in the present study.

The thermodynamic stimuli of reactions leading from a nucleobase-centered radical to product complexes (the O-P bond break) are significantly negative and the kinetic barriers of the particular steps of considered mechanism are sufficiently small to be overcome at the ambient temperature both in the gas phase and aqueous solution. Hence, the proposed mechanism might take place in the BrdG labeled DNA damaged with electrons.

Acknowledgements: The calculations have been carried out in Wrocław Center for Networking and Supercomputing (http://www.wcss.wroc.pl), grant No. 101486 and at the Mississippi Center for Supercomputing Researches.

Mechanism of the isopropyl radical induced degradation of DNA radiosensitizer. A computational and experimental study.

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Four brominated nucleosides, being DNA radiosensitizers: 5-bromo-2'-deoxyuridine (BrdU), 5-bromo-2'-deoxycytidine (BrdC), 8-bromo-2'-deoxyadenosine (BrdA) and 8-bromo-2'-deoxyguanosine (BrdG) were studied in UV irradiated water / isopropanol / acetone solution. In these systems the photons of 300 nm generate quantitatively the isopropyl radicals (ISOPs) which further react with bromonucleosides (BrdX). Hence, the considered reaction may provide a model for studying interactions between bromonucleosides and radicals, which should take place during radiolysis of water containing bromonucleosides or DNA labeled with BrdX.

The irradiation of solutions initiates the formation of the adduct of isopropanol and deoxynucleoside (isoprop-dX) as the main reaction products in all the cases. Furthermore, irradiation of brominated pyrimidine nucleosides leads also to 2'-deoxyuridine (dU) or 2'-deoxycitidine (dC), respectively. All these products were identified with high performance liquid chromatography and negative- and positive-ion mass spectrometry.

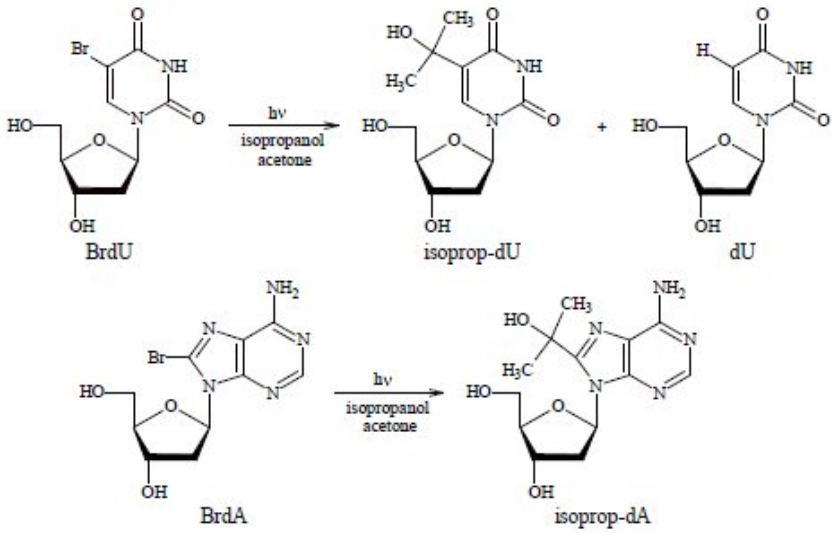

Fig. 1: Products observed after the irradiation of brominated pyrimidine (e.g. BrdU) and purine (e.g. BrdA) nucleosides.

In order to explain the mentioned above experimental findings, we modeled the mechanisms of bromoderivatives' degradation theoretically, applying the B3LYP method with the 6-31++G(d,p) basis set. Based on the thermodynamic and kinetic characteristics, derived computationally, we exclude the electron transfer process to be operative in the studied systems. A direct ISOP attack on BrdX was proposed instead.

Acknowledgements: This work was supported by the Polish Ministry of Science and Higher Education (MNiSW) under the Grant No. BMN/538-8221-1064-12 (J.M.) and by the Polish National Science Center (NCN) under the Grant No.: N N204 156040 (J.R.)

Mechanism of oxaliplatin binding to DNA

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Pt(II) drugs are currently extensively used against various types of tumors. Their antitumor activity comes from their interactions with DNA. They bound mostly to d(GG) moiety forming an intrastrand diadduct. Platination changes the DNA structure: the two GG bases are destacked and the DNA helix is bent. This distortion of DNA is then recognized by proteins. A bound protein may block the DNA chain being not accessible for e.g. transcription or replication. Oxaliplatin is a third generation platinum drug which is active against cisplatin-resistant tumors and has lower overall toxicity than cisplatin. We propose the mechanism of the binding of fully hydrolyzed oxaliplatin to ds(pGpG) dinucleotide in water solution. All stationary points along the reaction coordinate including the transition states were fully optimized by the RI-TPSS-D/COSMO/MWB-60(f)/def2-SV(P) method. Single point energy calculations on the optimized geometries were carried out by wB97XD/IEFPCM/MWB-60(2fg)/6-311+G(2d,2p)method.

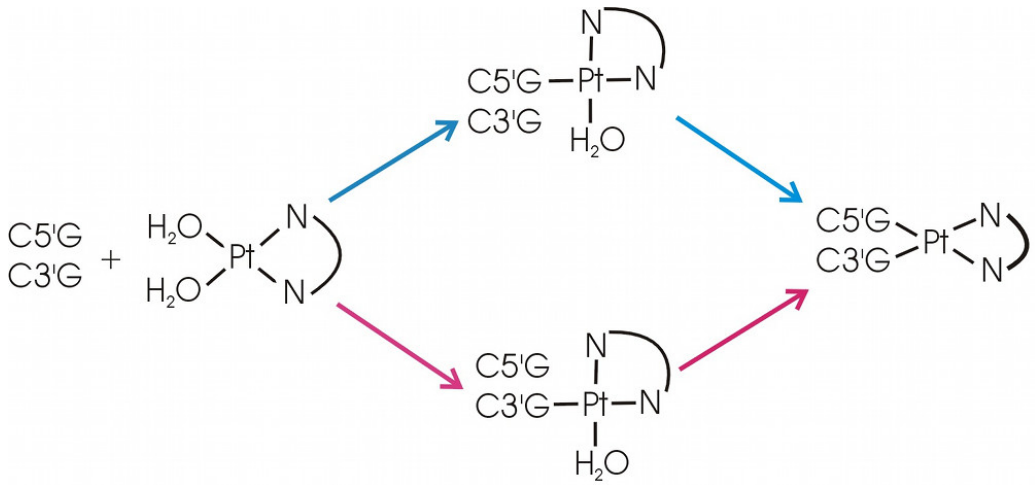

Fig. 1: Figure 1: Platinum diadduct with the GG sequence may be formed either via 5'G-monoadduct (5'G → 3'G binding direction: blue) or via 3'G-monoadduct (3'G → 5'G binding direction: red). Both pathways are considered in this study.

Acknowledgements: This work is supported by the Czech Science Foundation (grant No. 208/12/0622) and from the Ministry of Education, Youth and Sports of the Czech Republic (grant ME10149).

Binding of the organophosphorus pesticides by phospotriesterase: insight from classical and hybrid QM/MM simulations

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Phosphotriesterase (PTE) is among the most studied enzymes capable of biodegradation of neurotoxic organophosphate compounds, including agricultural pesticides. Despite a wealth of experimental and theoretical work on PTE, its catalytic mechanism has not yet been unequivocally determined. This research has been aimed at computational evaluation of the way PTE achieves its impressive rate enhancement. The knowledge of factors affecting substrate specificity and/or catalytic efficiency would allow for rational engineering of PTE mutants designed specifically to suit a broad range of purposes.

A reliable model of enzyme-substrate complex is an essential prerequisite required for the modeling of an enzyme-catalyzed reaction. Since no experimental structure of the former is available, the consecutive steps employed in modeling of PTE-substrate complexes are the subject of this contribution. In particular, classical molecular dynamics simulations along with hybrid QM/MM calculations will be employed to reveal molecular details of enzyme-substrate recognition along with their implications for the PTE catalytic properties.

Acknowledgements: The research was supported by Wrocław Research Center EIT+ under the project "Biotechnologies and advanced medical technologies-BioMed" POIG.01.01.02-02-003/08 financed from the European Regional Development Fund - Operational Program Innovative Economy, 1.1.2. Calculations were performed at Wrocław Center for Networking and Supercomputing.

Heterocyclic mono- and bisphosphonates as novel inhibitors for Parkinson's disease treatment

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Parkinson's disease is one of most common neurodegenerative disorders of a central nervous system. It is caused by the death of dopamine producing cells within the *substantia nigra*, which is located in midbrain. The primary symptoms of this disorder are tremors, rigidity, postural instability and bradykinesia. Currently there is no treatment to cure Parkinson's disease. There are several therapies, but all of them are designed to increase the dopamine level and alleviate the motor symptoms. The most effective way achieve this, is to administer L-DOPA in combination therapy with inhibitors of levodopa breaking down enzymes such as catechol *O*-methyltransferase (COMT), L-aromatic amino acids decarboxylase (AADC) and monoamieoxidase B (MAOB). According to the literature data, there are some libraries of catechol and nitrocatechol compounds that are able to inhibit the activity of above-mentioned enzymes. However they reveal high toxicity or they are unable to cross brain-blood barrier. This data have become a starting point for our investigations. We decided to design, synthesize and prepare a virtual screening of novel heterocyclic phosphonates and bisphosphonates towards they binding affinity to human COMT and MAOB active sites. The proposed compounds share common phosphonic unit that was investigated to bioisosterically mimic hydroxyl moieties in catechols that are being currently applied as therapeutics in Parkinsonism. In presented work flexible docking calculations were performed to gain an insight into the active site interactions responsible for enzyme inhibition. Since the docking results accompanied by molecular mechanics optimization suggested that several crucial active site residues interact with phosphonic group of ligand.

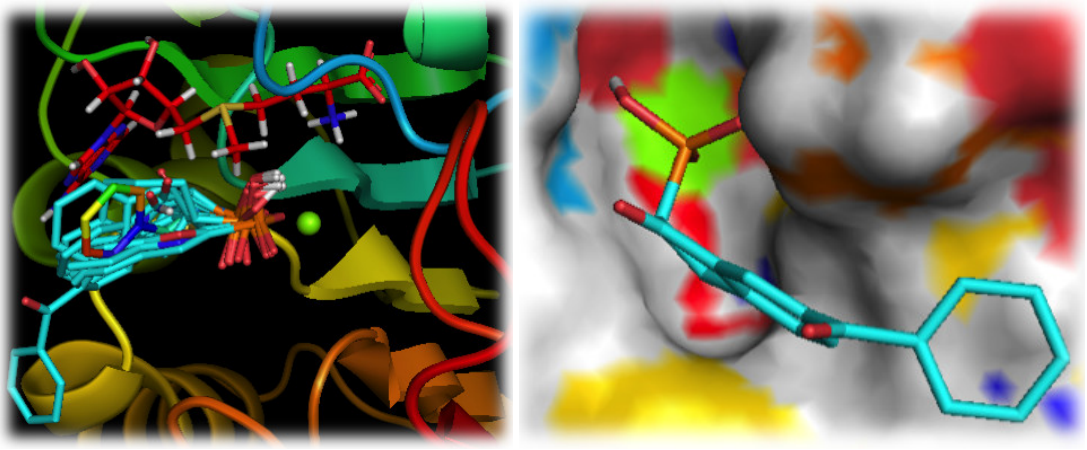

Fig. 1: Complexes between COMT and designed phosphonic inhibitors.

Acknowledgements: Calculations were performed at the Wrocław Center for Networking and Supercomputing and at the Institute of Applied Radiation Chemistry. Fellowship co-financed by European Union within European Social Fund.

Complexation of boronic acid with 1,2- and 1,3-diols – it is not as easy as it seems to be

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The importance, of boron containing compounds is increasing year by year in various areas of science starting from organic chemistry up to medicine. Boronic acids are able to form reversible covalent bonds with compounds containing 1,2- and 1,3-diol groups. This unique feature allows their application binding blocks of receptors designed for recognizing biologically active molecules such as: dicarboxylic acids, sugars, catecholamines or glycoproteins. Despite of many common applications of boronates there are still many questions concerning the mechanism and energetic profile of this process. The greatest controversy arises from determination, which form of boronic acid, trigonal or tetrahedral, is responsible for binding in aqueous solution and how the other factors such as solvent or buffer molecules may influence the reaction pathway.

Thus, we decided to investigate, how the substitution at boron center, and kind of diol molecules may influence the reaction energetic profile. In presented theoretical studies, phenylboronic, methylboronic, boric acid and dihydroxyborane were used as a model receptors able to complex three dihydroxy compounds: 1,2-dihydroxybenzene, 1,2–ethanediol and 1,3–propanediol. As a point of reference, to investigate the influence of the type of substituent at boron atom on diol complexation, we had selected dihydroxyborane. This choice was dictated by the fact that hydrogen atom cannot conjugate with vacant boron p orbital and molecule is lacking in resonance effect. Moreover, small difference in electronegativity between these two atoms makes also inductive effect neglected.

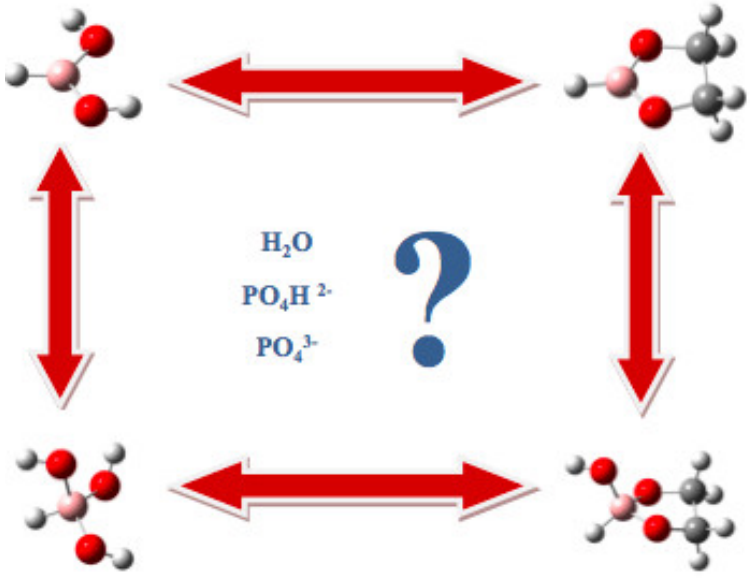

Fig. 1: Diols complexation equilibrium.

Acknowledgements: Calculations were performed at the Wrocław Center for Networking and Supercomputing.

Theoretical and experimental study of hydrogen abstraction from some chosen flavonoids

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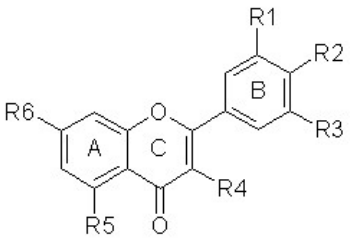

The flavonoids being studied are schemed in the Figure. The study consists of the two main groups of methods: theoretical and experimental which aim to quantify and predict antioxidant activity by free radical scavenging. The conformers of the flavonoids differing by the energy of intra-molecular hydrogen bonds were established in the study and so increased the number of the studied molecules. The all studied structures were subject of the systematic abstraction of hydroxyl hydrogen atoms and then the studied radicals were obtained by the sequence of PM3, HF/3-21G*, HF/6-31G(d), LSDA/6-31G(d) and B3LYP/6-31G(d,p) in the process of tight optimizations as spin doublets, followed by frequency computations at the HF/3-21G* and then at the final level. The radicals of each molecules can therefore be compared in their energies without taking into account any basis set correcting errors, as all the radicals of one molecule are elaborated in the same model chemistry UB3LYP/6-31G(d,p) in the same basis set. However, such elaboration is not enough to compare the energies of radicals of different molecules studied. As all the studied structures have hydroxyl group as R5 substituent, the G2MP2 theoretical thermodynamic study is carried out on bond dissociation of these hydroxyl groups to calibrate and gauge all the radicals in the family of the studied compounds in the computationally cheapest way. The supplementary computations SCRF IEFPCM in methanol are also done by the same methods and model chemistries.

Measurement of antiradical and antioxidant activity of extracts with DPPH free radical: Antiradical activity of extracts is measured by the method of Brand-Williams et al. [1]. DPPH solution **I** is prepared by dissolving of DPPH (2,2-diphenyl-1-picrylhydrazyl) radical in methanol (Merck, gradient grade) at 0.037 mg/ml. Solution **II** is prepared by dissolving of extracts in methanol (concentrations of extracts in sample depends on the antiradical activity of extracts). 11 ml of **I** solution will be preincubated at the temperature of 25°C for 5 min. Then 275 µl of **II** is added to **I** and carefully mixed. 2-ml samples are received at different time intervals depending on the activity of compound and absorbency is measured at 515 nm in glass cuvette with optical path equal to 1 cm. Control sample is prepared by the addition of 275 µl of methanol to the 11 ml of DPPH solution in methanol instead of extract addition, absorbency of control is measured at the same time as a sample. The antiradical activity is expressed as a number of antiradical units TAU_{515} by µmol of substance defined by Sroka and Franiczek [2].

Acknowledgements: Computations were performed at the Wrocław Center for Networking and Supercomputing.

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Vibrational optical activity spectra of organic compounds in the C-H stretching region

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Most organic compounds exhibit a strong vibrational optical activity in the C-H stretching region. So far, their spectra are only rarely used for structural studies as it is difficult to measure and interpret them. We measured Raman, Raman optical activity (ROA), infrared (IR) and vibrational circular dichroism (VCD) spectra of selected terpenes (camphor, fenchone and α-pinene) and compared them to theoretical simulations, in order to investigate how various computational approaches are able to describe these vibrations.

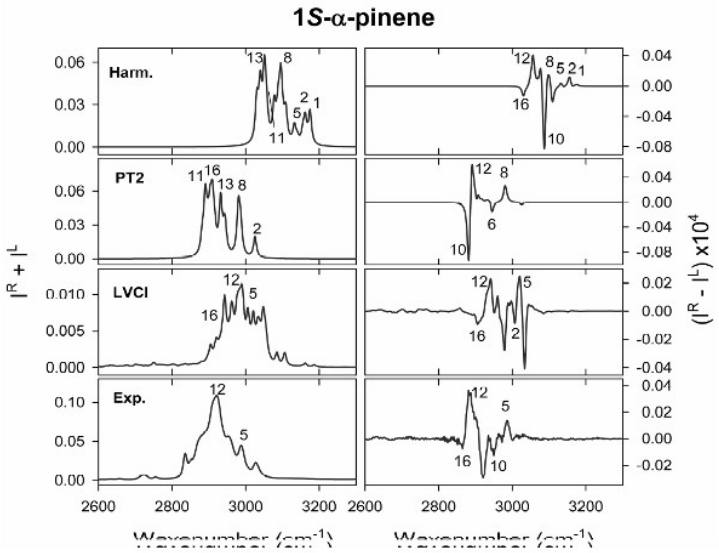

Fig. 1: Comparison of experimental Raman (left) and ROA (right) spectra of 1*S*-a-pinene in the C-H stretching region with different vibrational computational approaches.

Raman and ROA spectra were measured on the 514.5 nm ICP ROA spectrometer [1] in a wide wavenumber range (100-4000 cm^{-1}), including the C-H stretching region. Three different gratings were used. The IR and VCD spectra were measured with two instruments, optimized for the low and high frequency regions.

The C-H Raman and ROA spectral patterns appeared to be very sensitive to the computational model. Various density functionals, MP2 and combined electronic approaches and solvent models were tried. Second order perturbational (PT2) and limited vibrational configuration interaction (LVCI) computations were used for the vibrational problem [2]. The LVCI method provided the most realistic description of the spectra. The results show that current vibrational and electronic methods start to provide sufficient accuracy to interpret this spectral region, which can significantly broaden applications of vibrational spectroscopy.

Acknowledgements: Support from the Grant Agency of the Czech Republic (grant No. P208/11/0105), the Grant Agency of Charles University (grant No. 126310) and the Charles University in Prague (project SVV-2012-265304) is acknowledged.

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Variation of the electronic polarizability on the reaction path

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Electron dipole polarizability has been studied for the model reaction CO+HF using the IRC analysis. Polarizability of the system was calculated by the finite field method at the HF and MP2 level, with the 6-311G* and Sadlej pVTZ basic set. The maximum of polarizability has been observed near the point of the maximum softness Softest State (SS), as defined by Ordon and Tachibana [1]. This observation suggests, that important relation between electronic polarizability and softness, recently analyzed by Komorowski et al. [2, 3] is still operational within the IRC analysis. The SS is not identical with the transition state and no apparent relation has been found to the reaction force and the reaction electronic flux as proposed by Toro-Labbé [4].

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Conformational analysis of so called 'legal highs' using quantum mechanical models

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In the last past years, a increase In the availability of designer drugs has appeared on the drugs of abuse market in many countries [1]. The so called beta-keto or "legal highs" designer drugs such as flephedrone (4-fluor-methyl-cathinone) or mephedrone (4-methyl-meth-cathinone) [2]. Due to their chemical similarity to amphetamines or methcathinone and the use as alternatives for these drugs , a similar stimulant effect of the drugs could be postulated. Therefore, an intake of such drugs must be monitored in clinical and forensic toxicology and doping control. As many psychotropic drugs are extensively metabolized, they can be detected particularly in urine only via metabolites[[3–6].

Flephedrone is an analogue of cathinone - chemically similar to ephedrine, cathine and other amphetamines. Conformers of all isomers of flephedrone have been studied on quantum-chemical level. Calculations have been made using DFT and MP2 methods with two basis sets – 6-31G and 6-31G(d,p). Structural and thermodynamic data have been collected for all structures. All conformers have been connected through rotational transition states. Molecular potential energy surface for each molecule has been calculated.

Cathinone has been calculated using B3LYP and MP2 level of theory. Its metabolites – norephedrine and norpseudoephedrine – have been calculated as well. Cathinone has two low energy conformers. Norephedrine has four low energy conformers and norpseudoephedrine has three low energy conformers. All conformers have been connected with rotational transition states. All compounds have been calculated in solution. Solution has lowered their energies. Molecular Energy Potential Surfaces (MEPS) have been calculated for all low energy conformers to locate active site of molecules.

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Molecular dynamics study of phosphotriesterase-malathion complexes: influence of a single mutation on the substrate binding characteristics

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Phosphotriesterase (PTE) belongs to a group of enzymes acting on a variety of ester bonds in organophosphate compounds. Some of PTE potential substrates are widely used as pesticides (e.g., paraoxon, demeton S, parathion, malathion) or even as a biological weapon (e.g., sarin, tabun). The exact mechanism of reaction, leading to the hydrolysis of phosphoroorganic compounds, has not yet been discovered but the PTE catalytic activity, as well as possible factors affecting it, are under constant investigation. PTE-catalyzed hydrolysis of P-S bond is at least 4 orders of magnitude slower compared to the P-O bond cleavage [1]. It has been shown [2] that a single H254R mutation improves PTE ability to hydrolyze P-S bond in demeton S, while decreasing its catalytic activity toward P-O bond (paraoxon). As many organophosphate pesticides including malathion, a relatively poor PTE substrate [1], possess a thioester bond, it is of great importance to describe the molecular basis of how such a mutation affects the PTE catalytic activity.

Since experimental structure of PTE-bound substrate is not available, we used classical molecular dynamics simulations in order to model and evaluate interactions in PTE-malathion complexes. The latter include both wild-type enzyme and H254R mutant with an active site histidine replaced with arginine residue. The results will be discussed in terms of the impact of such a substitution on the malathion binding. Obtaining a reliable structure of an enzyme- substrate complex is also an important starting point for the modeling of an enzyme-catalyzed reaction.

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Molecular modeling of the kinetic enzymatic resolution of phosphoroorganic compounds

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The selective formation of enantiopure heteroorganic molecules is of fundamental importance in total synthesis of biologically active compounds. Although the number of stereocontrolled chemical reactions is constantly growing, many of the important molecules are still beyond reach of synthetic organic chemists. One solution is the use of enzymes. Naturally occurring enzymes are the most effective enantioselective catalysts, which are currently used even in industry. We would like to present the case study of the mechanism of the organophosphorus ester hydrolysis catalyzed by lipase CAL-B from *Candida antarctica*. Our recent results show that CAL-B is particularly effective in kinetic resolution of chiral phosphine oxides and its P-borane derivatives [1]. This fact inclined us to deeper studies on reactivity and enantioselectivity of lipase CAL-B towards P-chiral molecules. The crucial step of the enzyme-aided hydrolysis is the docking process - the formation of the protein-substrate reactive complex. The detailed investigation of the ligand-enzyme free binding energy was performed since it is a basic parameter influencing the enantioselectivity of the enzyme. The conformational flexibility of ligands was taken into consideration and was analyzed. Preliminary studies of the ligands [2] using QM methods and of the complexes and tetrahedral intermediates [3] allowed us to determine the favored configurations of the chiral substrates. Both experimental and theoretical results shows that oxide and P-borane phosphines undergo CAL-B – promoted hydrolysis with the same stereoselectivity. The main reason for that particular stereoselectivity of the substrates is the size of the biggest substituent on P-central atom, which preferentially is fitted in the biggest entrance pocket. Its placement inside the active site causes significant steric hindrance and leads to unfavorable conformations. The binding energy difference of the chiral complexes is significantly higher for phosphine oxides then for P-borane analogues what leads to its higher stereoselectivity of the enzyme toward phosphine oxides confirmed experimentally. The molecular modelling techniques have proved to be useful in explaining the stereochemistry of the CAL-B - promoted transformations and are in accord with the experimental results.

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Computational studies of new potential inhibitors of human type II inosine monophosphate dehydrogenase

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Inosine 5' monophosphate dehydrogenase (IMPDH), as key enzyme involved in the de novo biosynthesis pathway of purine nucleotides, is an attractive target for pharmacological intervention. Ribavirin (1-β-D-ribofuranosyl-1,2,4-triazole-3-carboxamide), being the substrate analogue of IMPDH, proved substantial antiviral activity. RMP (ribavirin 5'-monophosphate) competitively inhibits the enzyme and in consequence intracellular GTP pool is no longer sustainable for viral replication.

Recently, newly synthesized ribavirin analogues: 5-alkynyl-1,2,3-triazole nucleosides and their pronucleotides have been examined for their cytotoxicity towards human cancer cell lines [1]. Currently the compounds are tested for their antiviral activity.

Computational studies of ternary complexes of hIMPDH2 enzyme, a cofactor and 5'-monophosphate of 1,2,3-triazole nucleosides: ETCAR, ProTCAR or 5-bromo congener, respectively, as substrate will be helpful to rationalize differences in biological activity of studied compounds.

Acknowledgements: Support from grants No. MNiSW - N N519 405037 and MNiSW N N405 2516 33 is acknowledged. Calculations were performed at the Poznań Supercomputing and Networking Center and with PL-Grid Infrastructure.

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Force-field dependence of chignolin folding and misfolding: comparison with experiment and redesign

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We study the folding thermodynamics of chignolin using replica-exchange molecular dynamics with four different force fields: i) the AMBER ff03* [1] force field modified to match helix-coil data; ii) the AMBER ff03w [2] force field, designed for use with the highly optimized TIP4P-2005 [3] water model; iii) the AMBER ff99SB [4] force field; and iv) the CHARMM 22/CMAP [5] force field. With all four force fields, chignolin folds to its native structure with a population comparable with experiment. However, we find a misfolded state with a population of 20-50% (depending on force field), in which Gly7 adopts a β_{PR} backbone conformation, rather than the intended α_{L}. By reweighting, we show that differences between the force fields can mostly be attributed to differences in glycine properties. We find that including the misfolded structure in the 300 K ensemble in the most cases results in slightly improved agreement with experiment than parameters calculated from a folded ensemble only.

Although the likely fast timescales of interconversion of the folded and misfolded state would make its direct experimental detection challenging, we have instead redesigned chignolin to provide a reference peptide that should be truly two-state. We show by NMR and circular dichroism spectroscopy that the G7K mutant of chignolin, in which formation of this misfold is possible, is well folded with stability similar to the wild-type and does not populate the misfolded state in simulation.

Our results highlight the complexity of interpreting NMR data for small, weakly structured peptides in solution, as well as the importance of accurate glycine parameters in force fields, for a correct description of turn structures.

Acknowledgements: The authors gratefully acknowledge the support by the Operational Program Research and Development for Innovations - European Regional Development Fund (project CZ.1.05/2.1.00/03.0058), the Operational Program Education for Competitiveness - European Social Fund (project CZ.1.07/2.3.00/20.0017), and Integration of Regional Center of Advanced Technologies and Materials into International Networks of Nanotechnological and Optical Research (project CZ.1.07/2.3.00/20.0058).

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Modeling the structure of human interferon gamma c-termini

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Human interferon gamma (hIFN-γ) is an important signaling molecule, which plays a key role in the formation and modulation of immune response and in gene activity regulation [1]. The protein represents a non-covalent homodimer of 144 amino acids long monomers, organized in six α-helices, which are linked by short unstructured regions, followed by a long unstructured C-terminal domain (the last 21 amino acids) [2].

The hIFN-γ expresses its activity through the high-affinity interaction with its own species-specific extracellular receptor (hIFNγR). Three regions of the hIFN-γ molecule are responsible for receptor binding, one of which is a short sequence in the C-terminal tail (residues 128–131). The hIFN-γ C-terminal region is highly positively charged and therefore highly susceptible to proteases. Experimental studies demonstrated that removal of up to 9 residues causes gradual increase in the activity of the protein. However, the complete removal of the flexible C-terminus inactivates the cytokine. Although all studies undoubtedly proved the modulating effect of the unstructured C-terminal region on hIFN-γ activity, they failed to explain the molecular mechanism of its action due to the lack of X-ray diffraction data.

The extremely controversial conclusions about the function of the hIFN-γ C-terminus as well as the lack of a reasonable model explaining its role in the receptor binding prompted us to model its structure by means of molecular dynamics (MD) simulations. This structure was then used for investigating the interaction of hIFN-γ with hIFNγR1 to reveal the mechanism of this interaction and to shed more light on the role of the C-terminus in hIFN-γ – hIFNγR1 binding.

We performed extensive MD folding simulations (200 ns each), which unambiguously show that the C-termini tend to adopt a compact conformation together with the globular part of the cytokine. The obtained trajectories were then subjected to cluster analysis in order to detect the population intensity of the various conformational states. Analysis of the solvation free energy of the centroids of the most populated clusters confirmed their energetic favorability. For validation of the obtained results, the same simulations were performed with different simulation packages and force fields (GROMACS 4.5.4 and NAMD 2.9, resp. GROMOS 53a6, AMBER 99SB and CHARMM 22). Despite the expected variations in the details, our conclusions remained unchanged.

Acknowledgements: Support from Grants DCVP 02/1/29.12.2009 and DMU 03/23/12.12.2011 of the Bulgarian National Science Fund is acknowledged. Calculations were performed at the Bulgarian Supercomputing Center.

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Which DFT Methods should we choose for predicting the molecular structures and vibrational spectra of new platinum(II) anticancer agents?

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Cisplatin and carboplatin belong to the most successful anticancer drugs, however their toxic side effects and acquired cellular resistance have motivated the search for other platinum agents. One of the new developed promising drug is picoplatin, *cis*[$PtCl_2(NH_3)$(2-picoline)] which shows remarkable activity in the treatment of SCLC, a very aggressive form of the lung cancer. The derivatives of this compound are currently under investigation.

Density functional theory calculations can greatly facilitate the design of novel platinum agents. Accurate predictions of the geometric parameters, vibrational frequencies and IR(Raman) intensities complemented with the experimental studies of vibrational spectra can be used for determination of the molecular structure of a new compound.

In our previous study on cisplatin and carboplatin [1] we have shown that ab initio MP2 method is not recommended for predicting molecular geometries and vibrational frequencies of platinum complexes, while the mPW1PW density functional is clearly superior to B3LYP and MP2 methods in calculations of the vibrational spectra [1–3].

In this work we have compared the performance of several density functional theory methods for predicting the structural and vibrational properties of cisplatin and picoplatin. The tested functionals included: M06, M06-2X, M06-L, B2-PLYP, mPW1PW, PBE0, LSDA, B3LYP and CAM-B3LYP combined with different basis sets and effective core potentials for platinum. The results show that the M06-type methods overestimate the Pt-Cl bond lengths. In addition, the M06-L and M06-2X functionals predict too low frequencies of the υ(Pt-N) stretching vibrations, by about 70 cm^{-1}, in comparison with experiment.

Of all the investigated DFT methods, PBE0 and mPW1PW are the best performing functionals for calculations of the molecular structures and vibrational spectra of platinum(II) complexes.

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Nanomechanics of β-rich domains proteins related to neuronal disorders

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The beta sheet (β) is one of the most important proteins' secondary structure element. This type of structure ubiquitous: it occurs in enzymes, cell adhesion molecules or receptors, and often that type of structural arrangement is critical for a protein function. Particularly interesting are the neuronal β-rich proteins. Their defects in these biopolymers, or lack of them, may lead to severe neuronal disorders such as autism spectrum disorder, schizophrenia, Down Syndrome or Parkinson's disease.

Understanding the mechanical properties of such protein structures helps to elucidate their functions and possible aberrations. We used the Steered Molecular Dynamics (SMD) method [1] in order to better understand the influence of mechanical stress in β-rich protein domains present in neurons.

We have obtained 22 explicit solvent all-atom MD trajectories using the NAMD code (300 ns) and 20 implicit solvent coarse-grained simulations (770 ns) using the CHARMM program for LNS domain of neurexin, FnIII contactin domain, FnIII fibronectin domain and β-rich motif from fibroins. These structures systematically differ in the number of beta strands. We estimate correlation between the mechanical strength and the the number, topology and "evolutionary design" of beta strands.

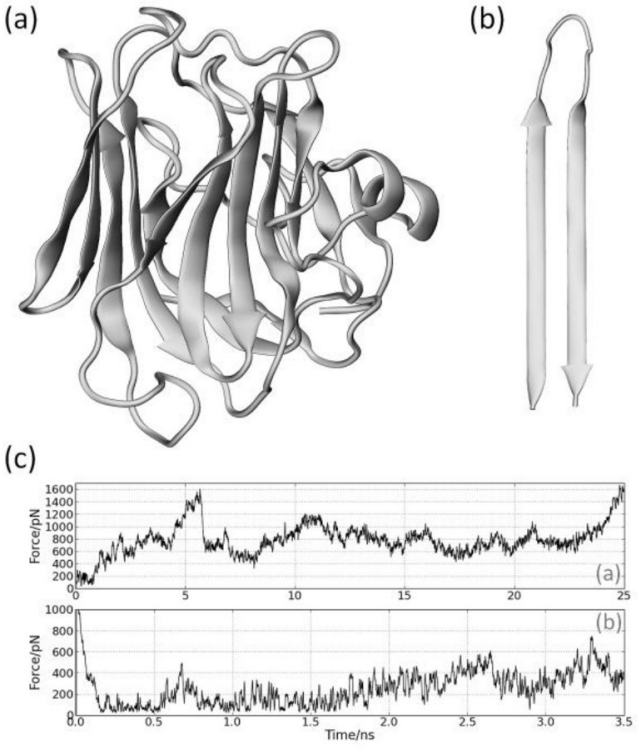

Fig. 1: β-rich structures: LNS domain of neurexin (a) and β-rich fibroin motif (b), and force time curves form all-atom SMD simulations (c).

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Theoretical study for predicting 3D structures of mosquito olfactory G-protein coupled receptors

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Malaria is a dangerous blood disease that is transmitted by infected mosquitoes. This is a severe and well-known problem especially in tropical regions of the world. According to the World Malaria Report 2011 there were about 216 million cases of malaria and an estimated 655 000 deaths in 2010. Most deaths occur among children living in Africa.

There are few ways in fighting with malaria: diagnosis, treatment and prevention. One way of prevention, the least destroyable to the natural environment and probably the best strategy for human protection, is repelling of mosquitoes. Probably the most popular insect repellent is a DEET though a toxicity of that compound has been reported in a number of cases. Additionally, despite a common usage of DEET since 1950s, we still do not know its mechanism of action. The latest investigations report about new insect repellent, VUAA1 [1,2], which may be thousand times stronger than DEET.

The complex molecular mechanism of the mosquito olfaction has been studied by a scientific community all other the world [3–5]. In the first step of the olfactory pathway the odorant molecules bind to odorant receptors (ORs) in the olfactory cilium which pass forward the signal to higher-order brain regions via special neurons. In order to study the mosquito repellent mechanism of action we need to know the relationship between mosquito repellents and olfactory receptors for which there is still no structural data.

The recent discovery of new olfactory mosquito gene families in Anopheles Gambiae [6,7] and Aedes aegypti [8] brought new insights into the mosquito olfaction. Noteworthy, Zweibel et al. have indicated a family of 79 putative OR proteins using bioinformatics tools in the Anopheles Gambiae genome [6]. ORs belong to the GPCR superfamily - therefore their structure contains seven transmembrane domains [9] and can be modeled using templates of other crystallized GPCRs.

In this work we focused on the prediction of 3D structures of all odorant receptors which create the olfactory mosquito system in Anopheles Gambiae. The new GPCRM server [10], developed in Biomodeling group at University of Warsaw was used to predict 3D structures of these receptors in high-throughput way. Such a broad study will also help to better understand the olfactory signal transduction pathway of insect odorant receptors.

Acknowledgements: This research was supported by grant no POIG.02.03.00-00-003-09 "DOTACJE NA INNOWACJE"

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Influence of the Hofmeister-active salts on the interfacial properties of Trp-cage miniprotein: a computational study

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In a recent study, Dzubiella [1] pointed out that the effects of Hofmeister-active salts on the stability of simple model peptides (like charged Ala-based helices) can be simulated using non-polarizable force fields. In this study, we investigated the influences of kosmotropic and chaotropic ions on the structural stability of a more protein-like model peptide with a well-defined structure, the Trp-cage miniprotein. It is a 20-residue-long polypeptide showing several characteristic features of proteins, namely, it has a stabilizing salt bridge and a well-defined hydrophobic core. The principal effect of the presence of Hofmeister-active cosolutes is the increase or decrease of the surface tension at the water-protein interface [2]. In the case of chaotropic salts, the compact structure becomes less favorable, therefore a rise in the protein-water interface is implicated; on the contrary, the kosmotropic salts favor the more compact structure with the decrease of interfacial area. This effect has been widely investigated so far, however, the atomic level mechanisms are still not fully understood.

In our theoretical study, the Amber ff99SB-ILDN force field together with the ion parametrizations of Joung et al. [3] and Baaden et al. [4] were used for 300-ns MD calculations with fixed, as well as for three 600-ns-long REMD simulations with non-constrained solute geometry. In the investigated systems, we used pure water, water with NaF and NaClO4 in 1 M final concentration as solvents, respectively. The fixed-geometry calculations were used to examine the interfacial region of Trp-cage, mainly in terms of ion distributions at 300 K. For the characterization of changes regarding the structural stability at different temperatures, which were induced by the cosoluted salts, the REMD simulations proved to be a suitable tool. The state of Trp-cage miniprotein was characterized by the solvent accessible surface area and its fluctuations, both showing a sigmoidal behavior as a function of temperature. The alteration of interfacial surface tension induced by cosoluted ions was also calculated from the above-mentioned quantities in an appropriate range of temperature.

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Characterizing the micelle-bound conformations of the stereoisomers of antimicrobial peptide indolicidin

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Indolicidin is a cationic antimicrobial peptide (AMP) isolated from the bovine neutrophils [3], which shows a broad spectrum of antimicrobial activity against Gram(+) and Gram(-) bacteria, as well as fungi. Although, this AMP is well-known as a membrane-active molecule, its mode of action is not clearly understood. Indolicidin possesses a remarkable primary structure (*i.e.* H-ILPWKWPWWPWRR-NH_2), consisting of five Trp and three Pro residues, as well as of three basic (*i.e.* Lys and Arg) and two apolar (*i.e.* Ile and Leu) amino acids. Since this peptide contains Pro residues, it exists as an equilibrium mixture of eight different stereoisomeric forms, according to the *cis-trans* isomerism about three Xaa-Pro peptide bonds.

In order to characterize the micelle-bound conformations of the stereoisomers of indolicidin, molecular dynamics (MD) simulations were performed on peptide-micelle systems, applying the DPC [**?**] and SDS [**?**] micelles. After an initial geometry optimization, for each peptide-micelle system, first a 20-ns-long MD calculation with fixed geometry of solute, then a 120-ns-long MD simulation without restraints were carried out. To describe the insertion processes, the distances between the centers of mass defined on the heavy atoms of stereoisomeric peptides and micelles were measured as a function of simulation time. For the inserted conformations of stereoisomers, the occurring β-turn structures were identified, and the preferred rotamer states were determined in the case of the side-chains of amino acids. Nevertheless, intramolecular interactions (*i.e.* aromatic-aromatic, proline-aromatic and cation-p interplays) formed between the different groups of peptides, as well as intermolecular interactions evolved between the peptides and lipid molecules were identified.

Based on the results obtained by the MD simulations, it could be concluded that significant differences could be found between the stereoisomeric forms of indolicidin, concerning their insertion processes and micelle-bound conformations. Accordingly, the various stereoisomers could be characterized by typical structural features, however, differences could be detected not only for the stereoisomeric forms of indolicidin, but also for the two types of micelles.

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Performance of polarization-consistent (pc-n) basis sets in predicting accurate parameters of He_2, Ne_2 and Ar_2 in the complete basis set limit

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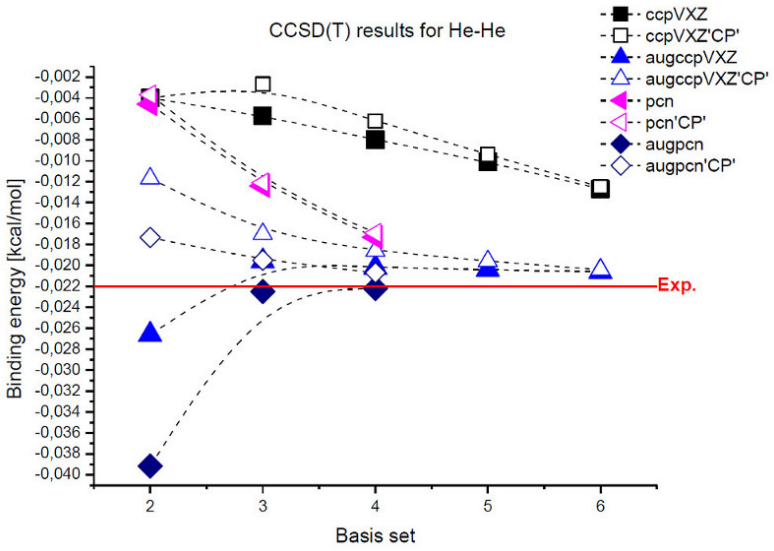
Real atomic systems are composed of atoms and molecules as result of delicate balance of attraction and repulsive forces. Formation of chemical bond and strong interactions, including hydrogen bonding is fairly accurately predicted by theoretical calculations at different levels of approximation. The presence of weak interactions in both biological systems and in modern materials is a great challenge for theoretical modeling. In principle, widely used Hartree-Fock ab initio method or popular B3LYP exchange-correlation hybrid density functional cannot properly handle dispersion forces. On the other hand, accurate ab initio methods are too expensive and cannot be used to describe systems containing hundreds of atoms. The only alternative in material sciences is therefore the DFT method with carefully selected or modified functionals, capable of predicting very weak hydrophobic forces. Despite their atomic closed-shell electronic structure, the noble gases exist as liquids at low temperatures. Therefore, the rare gas dimers are the simplest examples of the van der Waals complexes and very good models for testing the applicability of method for studying dispersion forces.



In this study, the performance of selected density functionals (mPW2PLYPD, B2PLYPD, wB97X, wB97XD, B972) was compared with benchmark CCSD(T) and MP2 results and available experimental data for He_2, Ne_2 and Ar_2 dimers.

Understanding boron atom Lewis acidity

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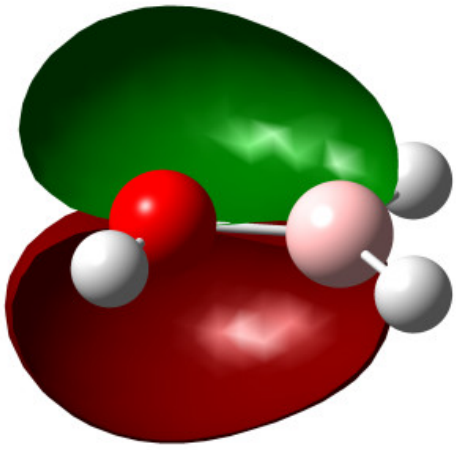

Form many years boron containing compounds are widely, and successfully used in supramolecular chemistry as a receptors for biologically active molecules and in crystal engineering. This particular application results from fact that boroorganic compounds posses vacant orbital p on boron atom, which may act as lone pair acceptor. Therefore, there is a great need to determine the parameters that are responsible for the boron atom acidity. We decided to examine which of the physicochemical properties of the molecules containing boron atom are responsible for their reactivity. In our theoretical studies borane have been chosen as a point of reference, this was dedicated by the fact that both resonance and inductive effect of the hydrogen atoms may be neglected. Through the addition of alkyl, aryl or hydroxyl substituent, or by their combination, we have examined their effect on the acidic properties of created molecules. During our investigations we considered such parameters as: charges, NBO population, molecular orbital energies and structural and energy changes after addition nucleophile to the investigated systems. This was done to determine the inductive, mesomeric and geometric effects of the substituents on the boron atom acidity.

Acknowledgements: Calculations were performed at the Wrocław Center for Networking and Supercomputing.

Mechanism of H-H activation by frustrated Lewis pairs. Insights from the analysis of domain averaged Fermi holes and generalized population analysis

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The recently discovered ability of the so-called frustrated Lewis pairs (FLP) to facilitate the activation of molecular hydrogen [1] has rapidly been recognized as new challenging paradigm for the design of environmentally-friendly metal-free hydrogenation catalysts. In past few years a lot of effort has been spent at exploring the wide synthetic potential of this new class of catalysts as well as at revealing of the mechanistic details of the reaction [3, 4]. The first mechanistic proposal by Stephan [2], assumed a stepwise character of the process, involving two possible scenarios differing in whether the reaction is initiated by H2 uptake via interaction with Lewis acid B center, or by the end-on interaction of H2 with Lewis base. More recently, a detailed computational study of the potential energy surfaces has suggested the existence of more favorable concerted reaction path involving the species which activates molecular hydrogen by simultaneous electron transfer from HH bond to acidic B center and donation of electrons from the lone pair of the basic site to antibonding *HH orbital. In order to contribute to the clarification of the existing uncertainties, we report in our study the insights into the electron reorganization along the IRC of the reaction as emerging from the analysis of domain averaged Fermi holes and the generalized population analysis. The above analyses have indeed confirmed the importance of concerted electron transfers, but the synergistic coupling of these transfers also revealed the extensive delocalization in the transition state of the reaction that can best be described in terms of multicenter bonding. Application of same methods on other reactions catalyzed by FLP confirms, that given model of activation is general and valid for C-H and other types of bonds.

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Optimization of analytical conditions of a fluorimetric method for the cortisol determination

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It is well known that many steroids can be converted at anhydrous and highly acidic conditions into dyes containing system of conjugated C=C bonds [1–3]. These reactions are of great importance from the analytical point of view.

Cortisol derivatization to fluorescent dye was carried out based on the procedure of Appel et al. [4]. According to this method cortisol assay is performed in solution containing methyl isobutyl ketone (MIBK), which enhance fluorescence [4]. Besides it is suitable solvent for cortisol extraction from water solution [4]. Although there are some papers dealing with fluorescence of steroids in mixtures containing H_2SO_4 and AcOH or Ac_2O [2–5], according to our studies, fluorimetric determination of cortisol should be carried out in mixture of MIBK and concentrated H_2SO_4, contrary to the suggestion that AcOH increase fluorescence [4]. Furthermore kinetic studies showed that spectra of samples should be recorded after at least 10 minutes of incubation.

It should be also taken into account that in biological samples other steroids can occur. We found that cholesterol is not fluorescently active under experimental conditions and hence does not interfere in cortisol analysis. Corticosterone, on the other hand after 50 minutes of incubation in MIBK/H_2SO_4 mixture, exhibits about two times higher fluorescence intensity than cortisol. Fortunately concentration of cortisol in human saliva and blood is higher than in case of corticosterone, what stands for potential applicability of tested procedure for efficient, fast and cost-effective method for measurements of this stress bio-marker. The theoretical rationale of observed fluorescence sensitivity on the reaction mixture composition is also provided based on molecular modeling.

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Topological analysis of electron density distribution in molecules containing a $\mathbf{N_2O_2}$ functional group

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Two nitrogen atoms and the same number of oxygen atoms can be fixed together in four different ways, if we assume that oxygen is two and nitrogen at most trivalence. N_2O_2 group could be four valence but a double bond in the molecule restricts the number to two substituents. Molecules with the N_2O_2 functional group are therefore derivatives of hyponitrous acid or nitric acid amide. The former include both diazoesters of hyponitrous acid, *N*-oxides, *N,N*-dioxides and *N*-nitrosohydroxyloamines, shown below:

R= –H, $–CH_3$, $–CH_2NH_2$, $–CH_2NO_2$

All structures are isoelectronic molecules, and each contains five two-center σ orbitals and four non-binding pairs. This follows from the geometry of forced trigonal sp^2 hybridization of nitrogen and oxygen atoms. The remaining three pairs of electrons are located on π orbitals. The $2p_z$ orbitals, with axes perpendicular to the plane of N_2O_2 group, generate four, four-center π–orbitals, two of which have a binding character. Thus, the electronic structure of those seemingly different molecules should be similar. The analysis of electron density distribution showed that compounds containing N_2O_2 functional group are characterized by a different distribution of electron density. All calculations were performed with Gaussian 09 [1]. The geometries were fully optimized and the harmonic vibrational frequencies were also calculated at the B3LYP level with 6-311++G(2d,p) basis set. The local topological properties of electronic charge density in the bond critical points were obtained using the Morphy98 program [2]. The Atoms in Molecules theory (AIM) [3, 4] has been applied to characterize the N-N and N-O bond nature in the investigated molecules.

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Structural form for early stage protein folding process simulation

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The success in protein structure prediction depends significantly on the starting conformation of the polypeptide under consideration. Usually the energy optimization procedure takes end in local minima. The random generation of starting structures generates very large sets of different structures. The cluster techniques are usually applied to identify the most probable structure.

The heuristic model for early stage protein folding process is presented. The introduction of limited conformational sub-space decreases the number of degrees of freedom for starting structural form of polypeptide to the extent balancing the amount of information carried by amino acid sequence with the amount of information necessary to define the early stage structural form.

The limited conformational sub-space (part of Ramachandran map) is characterized by the specific probability distribution for each amino acid. The seven local maxima are characteristic for all amino acids. Each local maximum identified by letter code makes possible the introduction of letter codes for early stage intermediate structural form (codes *A,B,C,D,E,F,G*). The contingency table (Tab.1.) collecting the probability of particular structure occurrence for particular amino acid sequence may be used for introductory structural form generation. The tetrapeptide is used as the unit since this length of polypeptide carry the recognizable secondary structure.

	ABCD	*ADEE*	*CCEG*	.....
ADGC	$p_{1,1}$	$p_{1,2}$	$p_{1,3}$	.....
ACTW	$p_{2,1}$	$p_{2,2}$	$p_{2,3}$	.....
.....	.....	.....	.....	.....

Table 1: Sequence-to-structure contingency table. The structural codes – italics, the sequence – bold.

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Recognition of dsRNA by HYL1 and DRB4 proteins from molecular modeling and molecular dynamics simulations

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Arabidopsis HYL1 and DRB4 are the double-stranded RNA-binding proteins that participate in RNA silencing pathways. HYL1 associates with Dicer-like 1 (DCL1) enzyme in generating microRNA. DRB4, the HYL1 homolog, interacts specifically with Dicer-like 4 (DCL4) and functions in the trans-acting siRNA pathway. The N-terminal fragment of both proteins comprises two tandem double-stranded RNA binding domains (dsRBD).

Experimental data have showed that HYL1 dsRBD1 is the major RNA binding site whereas HYL1 dsRBD2 binds to the DCL1. On the other hand it has been reported that DRB4 dsRBD1 specifically interacts with the DCL4 while DRB4 dsRBD2 is essential for both the dsRNA binding activity and the protein–protein interaction. Moreover, it was observed that HYL1 binds efficiently imperfect double-stranded RNA molecules, whereas DRB4 only binds perfect RNA duplexes, thus it has been suggested that HYL1 has intrinsic RNA binding specificities distinct from DRB4.

Recently, both crystal and solution NMR structures were solved for free HYL1 dsRBD1 and dsRBD2 domains as well as crystal structure for HYL1 dsRBD1/RNA complex [1, 2]. Experimental structures for any of DRB4 domains are not available so far.

Fig. 1: Homology model of DRB4 dsRBD2 in complex with dsRNA.

Using homology modeling we obtained structure of DRB4 dsRBD2 and constructed the DRB4 dsRBD2/dsRNA complex (Figure 1). To learn more about dynamic and structural differences in dsRNA binding between HYL1 dsRBD1 and DRB4 dsRBD2 domains we performed molecular dynamics (MD) simulations for both complexes. We compared the dynamics, hydrogen-bonding occupancies and solvent interface between the protein and RNA in both complexes.

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A molecular dynamics study of lunasin peptide

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Lunasin, a 43 amino acid peptide suppresses chemically induced transformations in mammalian cells and skin carcinogenesis in mice. This peptide has also been reported to exhibit very good bioavailability after its oral administration. However, despite its biological and medicinal significance, the exact three dimensional (3D) structure of lunasin is thus far not yet fully characterized. The present study involves the utilization of MD simulations to fully explore the conformational profile of a novel cancer-preventative 43 residue lunasin peptide, starting from an extended structure. For this purpose, a 300 ns MD simulation was performed using the GBOBC approximation under implicit solvent conditions. The aggregated information obtained from the analysis indicates that the lunasin peptide adopts three separate α-helical regions in its structure intervened by some unstructured or extended residues. However, the last few residues of both N-and C-terminus remain extended or unstructured. Moreover, the cell adhesion motif (RGD) plays a role of hinge winding and unwinding the central and C-terminus helical regions of the peptide. It is believed that the α-helicity associated with C-terminal aspartic acid residues of lunasin play a recognition role in its binding with the chromatin residue and could thus be responsible for its antimitotic action in the mammalian cell lines. The structural information obtained from the present study could be helpful to better understand the bioactive conformation of lunasin for future investigations, and can be further used in the design of new anti-cancer peptides with similar activity profiles.

Acknowledgements: The financial assistance from the Durban University of Technology and National Research Foundation (NRF), South Arica is gratefully acknowledged.

Molecular mechanisms of the photostability of 2-aminooxazole – a plausible RNA precursor on early Earth

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Even the simplest forms of life exhibit extreme complexity when it comes to the molecular structures responsible for their functions. On the other hand, all of those structures consist of a rather limited group of small molecules which are known as *the building blocks of life*. Probably the most fundamental question is why these compounds were chosen and others were eliminated in the early stages of biogenesis. It is plausible that persistent UV irradiation was one of the most significant environmental factors influencing this selection, indicating that biologically important molecules shall be quite resistant to the destructive effects of sunlight. Within the past two decades, numerous research groups proposed several molecular mechanisms which enhance the photostability of biomolecules including Watson-Crick base pairs and small peptides.

The knowledge gathered in the investigation of the photostability of nucleobases can be transferred to the problem of the origins of RNA, which is nowadays believed to be the most relevant carrier of genetic information in early living organisms. In 2009, Powner et al. suggested a reaction sequence leading to pyrimidine ribonucleotides under prebiotically plausible conditions via a small aromatic intermediate – 2-aminooxazole [1]. Since the prolonged irradiation was one of the key factors considered by Powner et al., we have chosen this intermediate as the subject for the investigation of the possible radiationless decay pathways. Vertical excitation energies, potential energy surface scans and *ab initio* based surface-hopping molecular dynamics simulations are presented and are shown to provide insight into the photochemistry of the title compound.

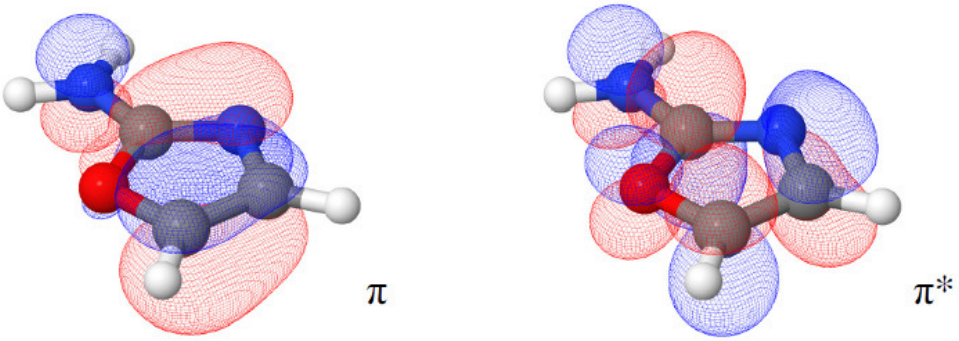

Fig. 1: CASSCF natural orbitals corresponding to the π→π* transition in 2-aminooxazole.

[1] Powner, M. W.; Gerland, B.; Sutherland, J.D., *Nature* **2009**, 459, 239-242.

The mechanism of phosphate catalysis of 2-aminooxazole formation in prebiotically plausible conditions

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Scientists speculate that one of the most important roles in prebiotic biogenesis could have been played by a polymer, which served to hold information and provided catalytic activities. According to the 'RNA world' hypothesis [1], this informational polymer was RNA. The arguments supporting the thesis are so-called 'molecular fossils' – essential sequences of RNA that regulate many significant processes in contemporary organisms. Nevertheless, the intuitive assumption that RNA chain components (ribonucleotides) must have formed from a ribose sugar, a nucleobase and phosphate seemingly ruled out this possibility. Particularly since, it has been proven that the synthesis of nucleosides from sugar and nucleobase is highly inefficient.

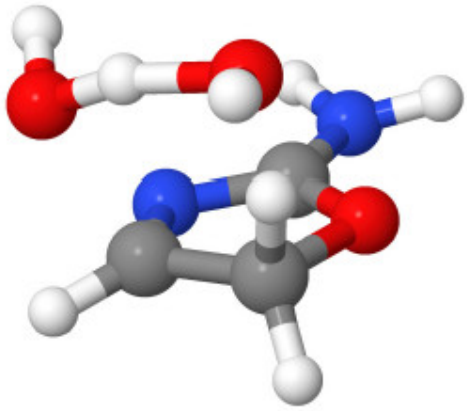

Fig. 1: Drawing showing the last transition state of the water-assisted reaction that leads to the final product.

In 2009 Powner et al. [2] suggested an alternative assembly mode for pyrimidine ribonucleotides. The route to activated cytosine ribonucleotide contains the traditionally assumed substrates (mixture of simple sugars and derivatives of cyanide and ammonia), which were used earlier in the successful synthesis of free nucleobases and ribose. Furthermore Powner et al. [2] introduced inorganic phosphate in the reaction mixture from the very beginning – not only in the last step to form the final product. Interestingly, phosphate proved extremely useful, serving as a catalyst to accelerate the slow steps and a buffer that could keep a roughly neutral pH.

The study focuses on the water-assisted mechanism of 2-aminooxazole formation, being the key intermediate in Powner's protocol, and shows possible mechanisms of phosphate catalysis as a comparison. The respective transition states, intermediates and complexes of reactants where found using different levels of theoretical approximation – including Møller-Plesset perturbation theory (MP2) and Kohn-Sham Density Functional Theory (KS-DFT) .

[1] Gilbert, W. *Nature* **1986**, 319, 618.
[2] Powner, M. W.; Gerland, B.; Sutherland, J. D. *Nature* **2009**, 459, 239–242.

Binding $Pt^{IV}(dach)Cl_4$ to GMP and followed-up reduction of platinum leaded to formation of $Pt^{II}(dach)Cl_2$

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Platinum complexes are well-known anticancer drugs. Recently also several other transition metal compounds were proven active both in vitro and in vivo experiments. There is an effort in recent medicine to replace cisplatin complexes by drugs with smaller side effects. Our calculations focus on the reaction of 5'-dGMP (2'-deoxyguanosine-5'-monophosphate) and 3'-dGMP with a platinum complex $Pt^{IV}(dach)Cl_4$ (dach=diaminocyclohexane) which leads to formation of active complex $Pt^{II}(dach)Cl_2$.

The first step of the explored mechanism is the substitution reaction where a new complex with coordinate-covalent bond between platinum and nitrogen N7 of guanine is formed releasing chloride particle. In the next step (besides a possibility of a phosphate cyclization reaction, which would terminate the process- green pathway) oxygen of phosphate group is transfer to C8 site of guanine forming 8-oxoguanine in the case of both 5'-dGMP (blue pathway) and 3'-dGMP (red pathway). The Pt^{IV} complex is within this step simultaneously reduced to Pt^{II} complex. Subsequently the Pt-N7 bond is broken (as shown in Fig. 1). The final products represent $Pt^{II}(dach)Cl_2$ and 8-oxo-GMP [1].

We studied geometry parameters of all species involved in this quite complex mechanism. The reaction course is considered from the thermodynamic point of view. The structures were optimized at the DFT level with B3LYP functional in basis set 6-31G* and PCM/UA0 solvation model. The energy parameters were determined using the single-point calculations at the DFT level B3LYP/6-311++G(2df,2pd) with DPCM/scaled-UAKS solvation model developed in our laboratory recently [2].

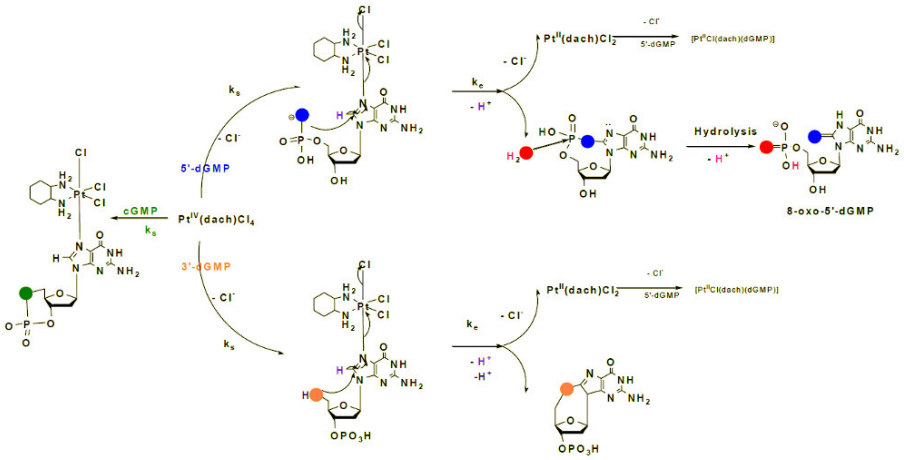

Fig. 1: 'Scheme of the explored reaction.

Acknowledgements: Support from GAUK grant No. 532212 is acknowledged. The access to the META Center supercomputing facilities is acknowledged.

[1] Choi, S.; Cooley, R. B.; Voutchkova, A.; Leung, C. H.; Vastag, L.; Knowles, D. E. *J. Am. Chem. Soc* **2005**, 127, 1773–1781.

[2] Zimmermann, T.; Burda, J. V. *J. Chem. Phys.* **2009**, 131, 135101.

Theoretical studies of calcium polyphenol glycosides interactions

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Effective dissolution of calcium oxalate, the main component of kidney stones, will allow the treatment the nephrolithiasis. The polyphenol glycosides are potential compounds to dissolve and inhibit formation of the kidney stones. These compounds have many oxygen atoms, which can interact with the calcium cation. The theoretical DFT investigation of polyphenol glycosides-calcium cation interaction was done to determine preferred structures and the role of polyphenol and carbohydrate part in the complex formation. Determination of the properties, which can characterize structure of the complex, will allow the design of a new compound more effectively interacting with calcium.

The interaction energy were calculated according the formula

$$\Delta E_{int} = E_{AB} - (E_A + E_B) \tag{1}$$

This work have shown that one of the most stable and the stronger interacting structures are glucoside of alizarin (Figure 1). The theoretical results are in accordance with complexing the calcium cation.

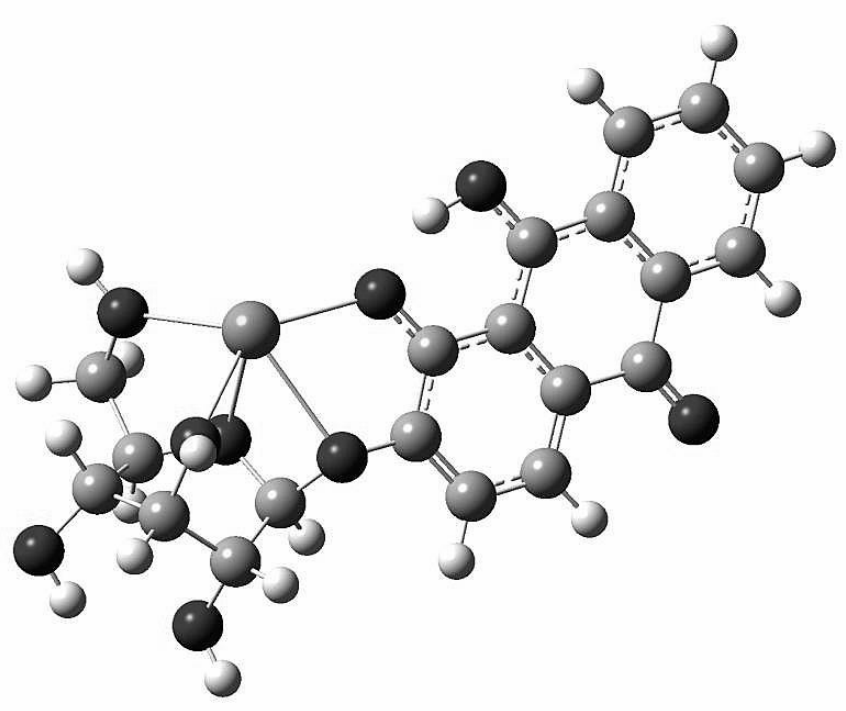

Fig. 1: Most stable and the stronger interacting structures for glucoside of alizarin

Acknowledgements: This work was supported by the Wrocław University of Technology grant. Thanks are extended to Wrocław Supercomputing and Networking Center.

Molecular modeling of bioactive coumarins and their metal complexes

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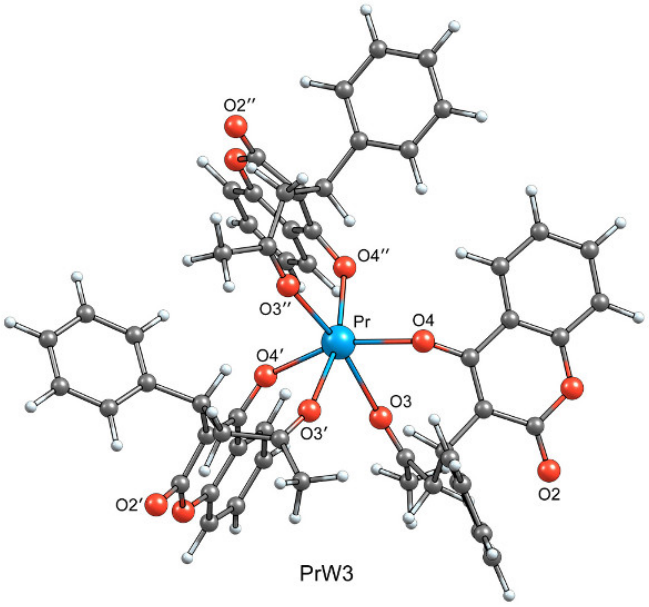

Both natural and synthetic coumarin derivatives have revealed a number of interesting biological properties and applications in biochemistry and medicine. The binding of coumarins to metal ions leads to formation of metal complexes with well pronounced activity, in some cases even higher than that of the isolated coumarins. The binding properties of coumarin ligands to metal ions are essential for understanding the factors controlling the biological activity of the metal complexes. In the present study the binding modes of a series coumarins (7-hydroxy-4-methylcoumarin (mendiaxon), coumarin-3-carboxilic acid (cca), 4-hydroxy-3-nitro-2H-chromen-2-one (hnc) and 4-hydroxy-3-(3-oxo-1-phenylbutyl)-2H-1-benzopyran-2-one (warfarin) to transition metal ions (Co(II), Mn(II), Zn(II), Ni(II)) and lanthanides (La(III), Ce(III), Nd(III), Pr(III)) were studied in details from first principles. Molecular structure modeling and spectra simulations (IR, Raman, NMR and electronic) are performed for the isolated coumarin ligands and for the metal complexes using high level ab initio methods (CCSD(T), CC2, MP2) and different DFT functionals (B3LYP, BHLYP, B3P86, B3PW91, PW91P86, MPW1PW91) and basis sets (6-31G(d), 6-31++G(d,p), SV(P), SV(P)D). The active binding centers of the neutral and deprotonated coumarin ligands are predicted by means of HOMO and molecular electrostatic potential values, calculated in gas phase and solvent using PCM reaction field. The most probable binding mode is suggested from energy calculations of series structural models. Natural bond orbital analysis and natural population analysis are performed to obtain the electron density distribution of the studied coumarin ligands. It was shown that DFT methods reliably predict the ground state geometry as well as the electronic and vibrational properties of the metal complexes.

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Rhodopsin cavity impact on retinal derivatives absorption properties

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Rhodopsin, also known as visual purple, is responsible for the perception of light in low-light conditions. The chromophore, 11-*cis*-retinal, consists of a β-ionone ring with a conjugated carbon chain covalently bound to rhodopsin via protonated Schiff base (PSB) linkage. Biological activity of rhodopsin is induced by photon absorption followed by isomerization of the 11-*cis*-retinal (PSB11) to its all-trans isomer (PSBT). The reaction, called photoisomerization, is one of the fastest observed so far (Fig. 1) [1].

Spectroscopic properties of 11-*cis*-retinal and its four methylated derivatives were investigated in the gas phase and in protein environment within *ab initio* and QM/MM techniques respectively. Ground state of PSBs were optimized within DFT and CASSCF levels of theory. Then energy evaluation of all models at the CASPT2 level was carried out. The active space included all valence π-orbitals and π-electrons, i.e. 12 orbitals and 12 electrons for all models. These calculations led to describe the influence of rhodopsin cavity on excitation energies of PSB11 analogs.

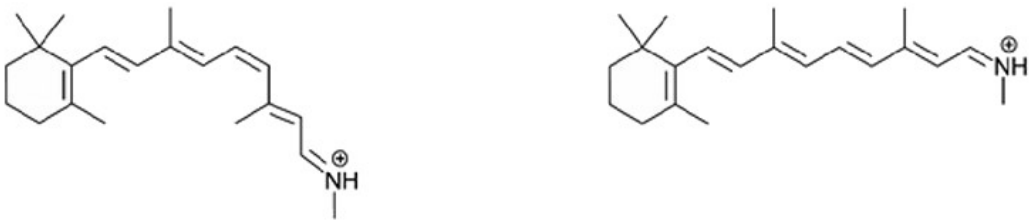

Fig. 1: Photoisomerization of PSB11 to PSBT.

Acknowledgements: The research was supported by Wrocław Research Center EIT+ under the project „Biotechnologies and advanced medical technologies" – BioMed (POIG.01.01.02-02-003/08) financed from the European Regional Development Fund (Operational Program Innovative Economy, 1.1.2). Calculations were performed at Wrocław Center for Networking and Supercomputing.

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Extending the range of FRET – the Monte Carlo study of the antenna effect

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Förster Resonance Energy Transfer (FRET) is the radiationless transfer of energy occurring between excited molecule (donor) and ground-state molecule (acceptor) via long range dipole-dipole interaction [1]. FRET plays an important role in all fields of science in which fluorescence phenomena are used, especially in understanding molecular biophysics. The features making FRET so widely used are a strong distance and orientation dependence, which creates a possibility to use it as a "spectroscopic ruler" to measure intermolecular distances.

One of the most challenging problems in using FRET in this way, is that the usable range of the interaction does not exceed 10nm, since the FRET efficiency strongly decreases with the increasing distance. Seeking ways to allow the use of FRET at longer distances is of great current interest.

We want to propose the advanced Monte Carlo analysis of, so called, antenna effect [2,3]. In this approach the single acceptor molecule is replaced by many linked molecules to which resonance energy transfer is more probable, which can extend the usable range of FRET experiments. By means of Monte Carlo simulations we mimic the biological antenna systems, what can be a powerful tool in understanding the geometry of system, underlying the peculiar FRET efficiency distribution. The results of numerical simulations are compared with the experimental ones

Acknowledgements: This research has been partly supported within the International PhD Project "Physics of future quantum-based information technologies" (MPD/2009-3/4) financed by Foundation for Polish Science.

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Solvent effects on the conformational preferences of model peptoids

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One of the most interesting ideas of the last several years was the proposal to shift the typical amino acid side chains from the α-carbon atom to the nitrogen atom of the peptide bond. Compounds formed in that way can be considered as oligomers or polymers of N-substituted glycines. They are called peptoids, and are capable of folding into helices or β-turns that mimic peptide structure and function.

This work describes the investigations into conformational properties of model peptoids: Ac-N(Me)-Gly-NHMe and Ac-N(Me)-Gly-NMe2. The research was performed by using the MP2/6-31G*//B3LYP/6-31G* method to calculate conformational Ramachandran maps and MP2/6-311++G** to optimize the conformers minima.The polarizable continuum model (PCM) was applied to estimate the effect of solvation on conformation. Energy minima of the Ac-N(Me)-Gly-NHMe and Ac-N(Me)-Gly-NMe2 have been analyzed in terms of the N-H···O, N-H···N and C-H···O hydrogen bonds and C=O dipole attraction. To validate the theoretical results obtained, conformations of the similar structures, gathered in the Cambridge Crystallographic Data Center (CCDC), were analyzed.

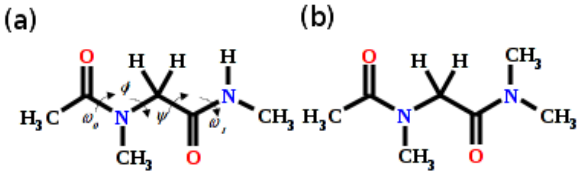

Fig. 1: General formula for Ac-N(Me)-Gly-NHMe (a) and Ac-N(Me)-Gly-NMe_2 (b).

The theoretical calculations show that interactions with solvent are very important for the conformational properties of the studied compounds. For both model peptoids the influence of water changes the number of conformers and reduces the energy difference between them. For both compounds with trans configuration of the N-terminal amide the helical conformations interact with the solvent the most strongly. However, for both cis isomers of the studied compounds, water has the strongest impact observed in the case of conformers F, which are characterized by torsional angles φ, ψ90° and 180° respectively.

The methylated peptide bond in peptoids reveals greater tendency to adopt the configuration cis. In vacuo, for both studied compounds the lowest energy conformer is in the trans configuration, and conformer with cis N-terminal amide bond has the energy about 2 kcal/mol higher, but in water the energy of this two isomers is almost equal. The difference in energy between them is 0.35 kcal/mol in the case of Ac-N(Me)-Gly-NHMe and 0.16 kcal/mol in the case of Ac-N(Me)-Gly-NMe_2.

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Predicting and interpreting the second-order nonlinear optical responses of fluorescent proteins: a challenge for quantum chemistry?

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[2] Center of Microbial and Plant Genetics, University of Leuven, Kasteelpark Arenberg 20, B-3001 Leuven (Belgium)
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[4] Institute for Nanoscale Chemistry and Physics, University of Leuven

Second-harmonic imaging microscopy (SHIM) is a new nonlinear optical (NLO) imaging technique. In particular, fluorescent proteins (FP's) covering the full rainbow of visible colors while displaying enhanced NLO properties constitute a "useful tool" for the characterization of living environments such as cells. In this work, on the basis of measurements of the second-order NLO responses on a set of six fluorescent proteins (eGFP, eYFP, eYFP Y203F, DsRed, zFP538, and mCherry) we have carried out a quantum chemical investigation of their first hyperpolarizabilities (β), the molecular property at the origin of the second-order NLO responses.

First, the second-order nonlinear optical properties of this set of FP's were experimentally determined by frequency-resolved femtosecond hyper-Rayleigh scattering [1]. Since these measurements were performed at a wavelength near resonance conditions, static β values were first extracted, not only to enable an easy comparison with experiment but also to provide intrinsic β responses. For this pre-treatment, three levels of refinement were considered within the two-state approximation (TSA). The first one is to consider only the crude TSA, which assumes that only one excited state contributes to the second-order NLO response, the second one consists in including an homogeneous damping in the TSA, while in the third one an inhomogeneous broadening based on the absorption spectrum is included to allow taking into account the vibronic structure of the excited states.

Several methods of calculations were employed to determine and analyze the first hyperpolarizabilities: the dynamic were obtained from the Time-Dependent Hartree-Fock (TDHF) scheme, the static by the Coupled-Perturbed Hartree-Fock (CPHF) method, and correlated ones using the MP2 scheme. The solvent effects are taken into account by using the Polarizable Continuum Model. TDHF/CPHF ONIOM calculations have also been carried out on larger systems to characterize the effect of the surrounding. Since values have been rarely calculated within the ONIOM procedure, TDHF and CPHF calculations were carried also out for the entire system and compared to the ONIOM results. Finally, we used the ONIOM MP2: HF method to make quantitative comparisons to experiment.

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What zeroth-order Hamiltonian for retinal chromophore CASPT2//CASSCF and CASPT2//DFT calculations?

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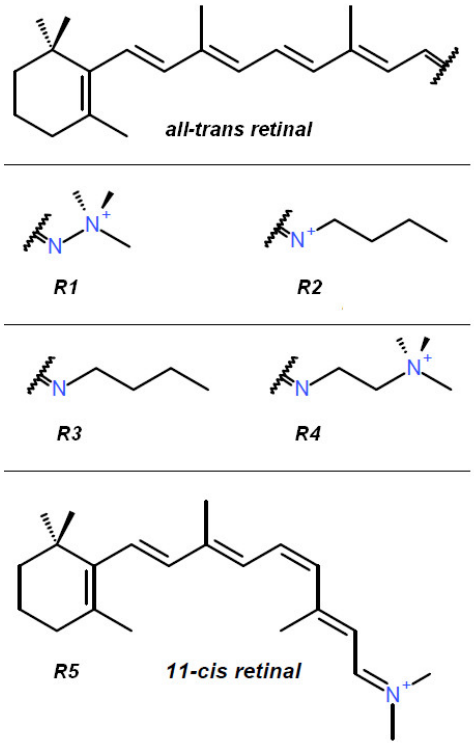
The phenomena of absorption of light, its conversion to other energy forms and sometimes finally emission are crucial for a lot of fundamental processes, that can be observed in live organisms.

An important example of situation, when a biological response is initiated by phenomenon of absorption of light can be observed in process of vision. It begins with light-induced photoisomerization of 11-cis retinal chromophore: 11-cis-retinal chromophore absorbs a photon and isomerises to the all-trans form.

In this work we examine absorption properties of retinal analogues (Fig. 1) that were selected following the availability of experimental spectral data [1–4]. DFT, CASSCF and CASPT2 computational methods were employed.



Nowadays developing of modern quantum chemistry methods to make them possible to predict real properties of molecules with a good accuracy is still necessary. For most small molecular systems CASPT2 is a state-of-the-art method. However it is significant to correctly choose the value of *IPEA-shift* parameter. This factor modifies the zeroth-order Hamiltonian and influence ionization potential and electronic affinity energies. The default value for most implementations of this method is 0.25 au, which is not always an optimal choice. In some cases, the non-default value of *IPEA-shift* seems to be a better choice.

In the present study we investigate the effect of *IPEA-shift* value on excitation energies in retinal analogues.

Acknowledgements: The research was supported by Wrocław Research Center EIT+ under the project „Biotechnologies and advanced medical technologies" – BioMed (POIG.01.01.02-02-003/08) financed from the European Regional Development Fund (Operational Program Innovative Economy, 1.1.2). Calculations were performed at the Wrocław Center for Networking and Supercomputing.

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On applicability of multiconfigurational perturbation theory to study spectral properties of GFP chromophore models

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Fluorescent proteins are important group of useful proteins that are often utilized for labeling biological specimens including even whole body imaging.

In this work we examine the spectral properties of the Green Fluorescent Protein (GFP) chromo-phore. Our calculations were performed for a group of model molecules (Fig. 1), that were selected following the availability of experimental spectral data [1–4]. DFT, CASSCF, and CASPT2 methods were used.

The main method used to calculate vertical excitation energies was second-order perturbation theory with complete active space self consistent field wavefunction (CASPT2). The influence of method-based equilibrium geometry on predicted excitations energies was discussed.

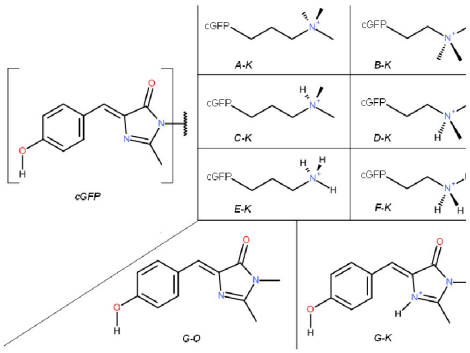

Fig. 1: Model chromophores used in the present work.

An important part of CASPT2 calculations is the choice of *IPEA-shift* parameter value. This factor modifies the zeroth-order Hamiltonian and influence ionization potential and electronic affinity energies. Currently, its default value in MOLCAS 7 program is 0.25 au. We are going to show, that it is usually needed to investigate the effect of *IPEA-shift* parameter value on calculated excitation energies. In our study this problem will be discussed in greater detail.

Acknowledgements: The research was supported by Wrocław Research Center EIT+ under the project „Biotechnologies and advanced medical technologies" – BioMed (POIG.01.01.02-02-003/08) financed from the European Regional Development Fund (Operational Program Innovative Economy, 1.1.2). Calculations were performed at the Wrocław Center for Networking and Supercomputing.

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Refinement of force field torsion parameters based on inclusion of conformation-dependent solvation effects – glycosidic torsion in nucleic acids

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The relevance of sampled structures and conformational dynamics of molecules in molecular dynamics simulations critically depends on the quality and accuracy of the applied empirical force field. One of the crucial components of any empirical force field is the torsion space parametrization. Torsion parameters are subject of constant refinement and have generated considerable research interest in recent years. Here we present a reparametrization of the glycosidic torsion angle chi of the Cornell et al. [1] force field for RNA simulations. Our approach is based on high-quality quantum mechanics calculations and incorporates some previously neglected solvation-related effects, which appear to be essential for obtaining correct description of the torsion space, namely the anti/high-anti balance. Resulting parameters are verified by extensive molecular dynamics simulations of canonical RNA duplexes and RNA hairpin loops. We show that our modification removes overstabilization of the high-anti region found in the ff99 force field and thus prevents formation of undesirable ladder-like structural distortions in RNA simulations. The refined chi parameters [2, 3] are now available as default parameters for RNA simulations in the latest version of the Cornell et al. force field (ff10).

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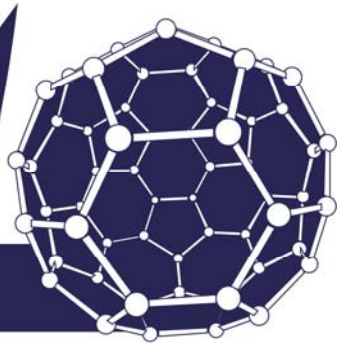

Mon Sept 10			**Registration**	
Tue Sept 11	**Advances and applications of computational methods** **L1:** A. Lagana **L2:** T. Wesołowski **L3:** W. Grochala **L4:** Z. Latajka	**Modeling molecular materials** **L5:** T. Clark **L6:** B. Szyja **L7:** A. Michalak	**Modeling Interactions in Molecular Materials** **L8:** M. Yáñez **L9:** J. Murray **L10:** J. Koca **L11:** M. Mitoraj **L12:** M. Jabłoński	**Poster Session A** **P1 – P45**
Wed Sept 12	**Advances and applications of computational methods** **L13:** A. Tachibana **L14:** A. Toro-Labbé **L15:** P. Politzer **L16:** P. Jaque	**Modeling molecular materials** **L17:** J. Sauer **L18:** B. Kuchta **L19:** O. Shishkin **L20:** A. Sikorski	**Panorama art gallery** **Wrocław sightseeing**	**Centennial Hall Discovery Center Show** **Japanese Garden** **Conference dinner**
Thu Sept 13	**Modeling biomolecules** **L21:** W. Minor **L22:** J. Polański **L23:** J. Gu **L24:** P. Paneth	**Modeling biomolecules** **L25:** J. Burda **L26:** J. Korchowiec **L27:** P. Dominiak **L28:** D. Rutkowska-Żbik **L29:** Ł. Pepłowski	**Poster Session B** **P46 – P91**	**Workshop – computational methods to determine electric dipole properties of molecules and their aggregates** **L30:** R. Góra & R. Zaleśny
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