SEMINÁŘ STUDENTŮ ÚFCH JH 2010

Konferenční centrum
AV ČR v Liblicích

18. - 20. 5. 2010

Seminář studentů ÚFCH JH 2010

Sborník příspěvků

ze studentské konference konané
18.- 20. května 2010
v Konferenčním centru AV ČR Liblicích

Seminar of Students of JHI 2010

Collection of abstracts

of all lectures given at the student conference
held on 18 - 20 May 2010
in Conference Centre of the Academy of Sciences
of the Czech Republic in Liblice chateau

Seminář studentů ÚFCH JH 2010
Sborník příspěvků ze studentské konference
konané 18.-20. května 2010
v Konferenčním centru AV ČR Liblicích

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SEMINÁŘ STUDENTŮ ÚFCH JH 2010

PROGRAM 1. dne konference - Úterý 18.5.2010

Odjezd autobusem z parkoviště před ústavem ve 14:00 hodin.

Předpokládaný příjezd do Konferenčního centra AV ČR v zámku v Liblicích v 15:00 (15:30) hodin.

Čas	Předsedající	Přednášející	Název
15:00 – 16:30	**Registrace a ubytování účastníků konference** **Občerstvení před zahájením konference** *(od 16:00 hodin v restauraci: káva, nápoje a zákusek)*		
16:30	**Zahájení konference „Seminář studentů ÚFCH JH 2010“ - prezentace studentů z mimosoutěžní kategorie a kategorie I a II.**		
16:40	***Květa STEJSKALOVÁ***	Jan KŘÍŽ *(SŠ student, Gymnázium AITIS Praha 4, školitelka M.Hromadová)* ***mimosoutěžní příspěvek-práce SOČ***	STUDIUM ADSORPČNÍCH VLASTNOSTÍ PESTICIDU ATRAZIN NA VYBRANÝCH PŘÍRODNÍCH MATERIÁLECH ZA POUŽITÍ POLAROGRAFICKÉ METODY
16:55		Vít SVOBODA *(SŠ student, MSŠCH Praha 1, šk. Ondřej Votava)* ***mimosoutěžní příspěvek-práce SOČ***	KONSTRUKCE A CHARAKTERIZACE DIODOVÝCH LASERŮ PRO ANALÝZU STOPOVÝCH MNOŽSTVÍ LÁTEK V PLYNNÝCH VZORCÍCH *Student se prezentace z důvodu skládání maturitní zkoušky nezúčastní, jeho práce však bude představena posterem a krátkým videoklipem natočeným v laboratoři.*
17:00		Alan LIŠKA *(bakalářské studium PřF UK, šk. J.Ludvík)* ***kat I***	ELECTROCHEMICAL REDUCTION OF MOLECULES WITH MORE REDOX CENTERS: MONO-, DI-, TRI- AND TETRANITROCALIX-[4]-ARENES AND THEIR MODELS
17:20		Pavel KOŠŤÁL (*bakalářské studium MFF UK; šk. M. Fárník)* ***kat I***	SBĚR A ZPRACOVÁNÍ DAT A OVLÁDANÍ EXPERIMENTU POMOCÍ LABVIEW
17:40	**PŘESTÁVKA**		
18:00	***Libor VEIS***	Jan SUCHÁNEK *(diplomant VŠB-TU Ostrava, školitel Z. Zelinger)* ***kat I***	LASEROVÁ FOTOAKUSTICKÁ SPEKTROSKOPIE V KONDENZOVANÉ FÁZI
18:20		Věra HUDSKÁ *(II. ročník, školitel-konzultant P.Janda)* ***kat II***	ELECTRODE COATING BY CHEMICAL MEDIATOR: THE AFM STUDY OF SURFACE NANOMORPHOLOGY
18:40		Viliam KOLIVOŠKA *(II ročník, šk. M.Hromadová)* ***kat II***	REDOX AND ELECTRONIC PROPERTIES OF MOLECULAR WIRES
19:00	**Ukončení prvního dne konference** **VEČEŘE v RESTAURACI - začátek v 19:15**		

PROGRAM 2. dne konference - Středa 19.5.2010

Čas	Předsedající	Přednášející	Název
8:55	**Zahájení druhého dne konference - prezentace studentů kategorie I. a II.**		
9:00	***Radek MACHÁŇ***	Mikuláš PEKSA *(diplomant MFF UK, školitel M. Kočiřík)* ***kat I***	INVESTIGATION OF MATTER TRANSPORT IN POROUS MATERIALS BY MEANS OF PFG NMR
9:20		Kristýna SOVOVÁ *(I. ročník PGS, školitel P. Španěl)* ***kat I***	SELECTED ION FLOW TUBE MASS SPECTROMETRY (SIFT-MS): FUMES OF EXPLOSIVES AND PLANT ODOURS
9:40		Petr KLEIN *(I. ročník PGS, školitel J. Dědeček)* ***kat I***	CHARACTERIZATION OF AL SITING IN ZEOLITES USING ^{27}Al (MQ) MAS NMR. EFFECT OF COUNTER-CATIONS ON ^{27}Al OBSERVED AND ISOTROPIC CHEMICAL SHIFT
10:00	**PŘESTÁVKA NA KÁVU**		
10:30	***Martin FERUS***	Marie KOLÁŘOVÁ *(diplomantka PřF UK, školitel Aleš Benda)* ***kat I***	DYNAMICKÁ SATURAČNÍ OPTICKÁ MIKROSKOPIE POUŽÍVAJÍCÍ SVĚTLEM PŘEPÍNATELNÉ PROTEINY
10:50		Helena DRAGOUNOVÁ *(bakalářské studium, LF UK; šk. P.Hrabánek)* ***kat I***	HYDROTHERMAL SYNTHESIS OF SMALL PORE ZEOLITE AFX (SSZ-16)
11:10		Aleš HAVLÍK *(I. ročník PGS, školitel M Horáček)* ***kat I***	MODIFIKACE POLOSENDVIČOVÝCH KOMPLEXŮ PRVKŮ 4B. SKUPINY ARYLAMINÁTOVÝMI LIGANDY
11:30	**PŘESTÁVKA**		
11:45	***Ludmila ŠIMKOVÁ***	Tomáš STEINBERGER *(I. ročník PGS, školitel M. Hof)* ***kat I***	FLUORESCENCE CROSS-CORRELATION SPECTROSCOPY AS A TOOL FOR STUDY OF INTERACTION BETWEEN THE UNILAMELLAR VESICLES AND THE PEPTIDES
12:05		Katarzyna SULISZ *(I. ročník PGS, školitel J.Čejka)* ***kat I***	METAL ORGANIC FRAMEWORKS IN ORGANIC SYNTHESIS
12:25		Barbora ŠUSTROVÁ *(II. ročník, šk. -konzultant V. Mareček)* ***kat II***	A STUDY OF CALIXARENE SELF-ASSEMBLED MONOLAYERS ON GOLD METAL SURFACES
	PŘESTÁVKA NA OBĚD *(OBĚD SE PODÁVÁ V RESTAURACI OD 12:45)*		
14:30	***David BEK***	Martin FERUS *(II. ročník, školitel S. Civiš)* ***kat II***	FORMATION AND DECAY OF HNC/HCN IN THE POSITIVE COLUMN DISCHARGE
14:50		Petr KUBELÍK *(II. ročník, školitel S. Civiš)* ***kat II***	INTERPRETATION AND MODELING OF TIME-RESOLVED IR SPECTRA
15:10		Libor VEIS *(II. ročník, školitel J. Pittner)* ***kat II***	QUANTUM COMPUTING APPLIED TO CALCULATIONS OF MOLECULAR ENERGIES: CH_2 BENCHMARK
15:30	**PŘESTÁVKA NA KÁVU A ZÁKUSEK**		
16:00	***Jan SKŘÍNSKÝ***	Ludmila ŠIMKOVÁ *(II. ročník, šk. J.Ludvík)* ***kat II***	DECOMPOSITION MECHANISM OF 1,1 DIAMINE 2,2 DINITROETHENE (FOX 7) A SPECTROMETRIC STUDY
16:20		Martin ŠTEFL *(II. ročník, školitel M. Hof)* ***kat II***	MULTIFREQUENCY – DOMAIN LIFETIME DATA ANALYSIS USING PHASOR PLOT APPROACH
16:40		Lukáš SOBEK *(II. ročník, školitel J.Pittner)* ***kat II***	FEMTOSECOND NON-ADIABATIC MOLECULAR DYNAMICS: A STUDY OF PHOTOCHEMICAL DEACTIVATION OF INDOLE MOLECULE

17:00		Václav Oborník *(VŠ student 1. ročníku FCHT VŠCHT v Praze, školitel M. Horáček)* ***mimosoutěžní příspěvek***	POLOSENDVIČOVÉ TITANIČITÉ KOMPLEXY OBSAHUJÍCÍ VAZBU KŘEMÍK-VODÍK
17:15	**UKONČENÍ DRUHÉHO DNE KONFERENCE.** *VEČEŘE V RESTAURACI OD 17:45 HODIN*		
17:20-17:35	**PRO ZÁJEMCE** ***mimokonferenční prezentace***	***K. Stejskalová***	***Představení výsledků projektu ÚFCH JH s názvem „Tři nástroje“ (MŠMT r.č.2E08038; 2008-2009) věnovaného vzdělávání studentů se zájmem o přírodní vědy a popularizaci výsledků V&V vědců z ÚFCH JH.***

PROGRAM 3. dne konference - Čtvrtek 20.5.2010

Čas	Předsedající	Přednášející	Název
8:15	**Zahájení třetího dne semináře - prezentace studentů kategorie II.**		
8:20	***Martin KUBŮ***	Jan SKŘÍNSKÝ *(III.ročník, šk. Z. Zelinger)* ***kat II***	ANALYSIS OF IODOMETHYL RADICAL, CH_2I ($\tilde{X}^2B_1$)
8:40		Lenka BERANOVÁ *(III. ročník, školitel M. Hof)* ***kat II***	OXIDATION CHANGES PHYSICAL PROPERTIES OF PHOSPHOLIPID BILAYERS
9:00		Miroslav ŠULC *(III. ročník, školitel-konzultant R. Čurík)* ***kat II***	ROTATIONAL EXCITATIONS OF POLAR MOLECULES BY COLD ELECTRONS
9:20	**PŘESTÁVKA**		
9:40	***Lenka BERANOVÁ***	David BEK *(III. ročník, školitel J. Čejka)* ***kat II***	IMMOBILIZED RUTHENIUM CATALYSTS FOR OLEFIN METATHESIS
10:00		Radmila JANEČKOVÁ *(III. ročník, školitel Z. Zelinger)* ***kat II***	STUDIES OF MOLECULAR SPECIES RELEVANT TO THE SAFETY ENGINEERING WITH AID OF SPECTROSCOPIC METHODS
10:20		Milan ONČÁK *(II. ročník, školitel P.Slavíček, šk. –konzultant M.Fárník)* ***kat II***	PROTEIN RADIATION CHEMISTRY: FROM AMINO ACIDS PHOTOSTABILITY TO DAMAGE OF TERTIARY STRUCTURE
10:40	**PŘESTÁVKA NA KÁVU A ZÁKUSEK**		
11:10	***Martin ŠTEFL***	Martin KUBŮ *(III. ročník, školitel J. Čejka)* ***kat II***	SYNTHESIS AND PROPERTIES OF NOVEL TNU-9, IM-5 AND SSZ-74 ZEOLITES
11:30		Milan MAŠÁT *(III.ročník, šk. O. Votava)* ***kat II***	SUPERSONIC DISCHARGE RADICAL SOURCE: NOZZLE GEOMETRY INFLUENCE ON THE OH RADICAL GENERATION
11:50		Radek MACHÁŇ *(IV. ročník, školitel M. Hof)* ***kat II***	A NOVEL ANTIMICROBIAL PEPTIDE ARENICIN-1 AND ITS LIPID-SPECIFIC INTERACTION WITH MODEL MEMBRANES
12:10	**UKONČENÍ PREZENTACÍ A CELÉ KONFERENCE.**		
SLAVNOSTNÍ VYHLÁŠENÍ VÝSLEDKŮ SE USKUTEČNÍ V PÁTEK 21.5. OD 10:15 HODIN V BRDIČKOVĚ POSLUCHÁRNĚ ÚFCH JH. OCENĚNÍ STUDENTŮM PŘEDÁ ŘEDITEL ÚSTAVU.			
12:30 14:00	**OBĚD V RESTAURACI od 12:30 hodin** **Odjezd do Prahy** - *autobusem z parkoviště u zámku ve 14:00* *(Návrat do Prahy k budově ÚFCH JH ca v 15-15:30 hodin.)*		

Účastníci semináře studentů ÚFCH JH 2010

Kategorie I (11)

Diplomanti a studenti magisterského studia, případně další zájemci z řad bakalářů (6)

Dragounová Helena (*bakalářské st. Školitel P. Hrabánek)*
Kolářová Marie *(diplomantka, školitel A. Benda)*
Košťál Pavel (*bakalářské st. MFF UK, stáž u .M. Fárník)*
Liška Alan *(bakalářské studium, školitel J.Ludvík)*
Peksa Mikuláš (*magisterské studium, školitel M. Kočiřík)*
Suchánek Jan (*diplomant., školitel Z. Zelinger)*

Studenti 1. ročníku PGS (5)

Havlík Aleš *(školitel M. Horáček)*
Klein Petr *(školitel J.Dědeček)*
Sovová Kristina (*školitel P. Španěl)*
Steinberger Tomáš *(školitel M. Hof)*
Sulisz Katarzyna *(školitel J. Čejka)*

V průběhu semináře své příspěvky z absolvované odborné roční stáže představí i nejmladší studenti z tzv. ***mimosoutěžní kategorie (3):***
*(abstrakty ve sborníku oznaļ eny ***)*

Jan Kříž *(3. ročník SŠ, Gymnázium Altis Praha 4, školitelka M.Hromadová)*

Vít Svoboda *(4. ročník SŠ, MSŠCH v Praze 1; školitel O.Votava)*

Václav Oborník *(1. ročník VŠ studia, FCHT VŠCHT v Praze; školitel M. Horáček)*

Kategorie II (18)

Studenti 2. ročníku PGS (10)

Ferus Martin *(školitel S. Civiš)*
Hudská Věra *(2.školitel P. Janda)*
Kolivoška Viliam *(školitel M. Hromadová)*
Kubelík Petr *(školitel S. Civiš)H*
Ončák Milan *(školitel P. Slavíček, 2. školitel M. Fárník)*
Sobek Lukáš *(školitel J. Pittner)*
Šimková Ludmila *(školitel J. Ludvík)*
Šustrová Barbora *(2. školitel V. Mareček)*
Štefl Martin *(školitel M. Hof)*
Veis Libor *(školitel J. Pittner)*

Studenti 3. ročníku PGS (7)

Bek David *(školitel J. Čejka)*
Beranová Lenka *(školitel M. Hof)*
Janečková Radmila *(školitel Z. Zelinger)*
Kubů Martin *(školitel J. Čejka)*
Mašát Milan *(školitel O. Votava)*
Skřínský Jan *(školitel Z. Zelinger)*
Šulc Miroslav *(2. školitel R. Čurík)*

Možnost prezentovat se naposledy mají i letošní studenti regulérního ***4. ročníku PGS studia – přihlášen (1):***

Macháň Radek *(školitel M. Hof)*

Hodnotící komise:

M. Hromadová
M. Horáček
J. Pittner

Celkem své prezentace přihlásilo 32 studentů.

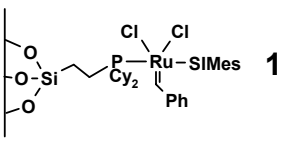
IMMOBILIZED RUTHENIUM CATALYSTS FOR OLEFIN METATHESIS

Ing. David Bek

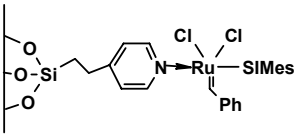
Prof. Ing. Jiří Čejka, DrSc.

Olefin metathesis is an important organic reaction with numerous applications in fine chemical synthesis[1]. Ru-based complexes are the most popular metathesis catalysts due to their high activity and tolerance to a variety of functional groups in substrate molecules. High cost of Ru complexes used and the demands on the product purity stimulate the development of Ru heterogenized catalysts, which enable easy catalyst - product separation and catalyst reusing. Mesoporous molecular sieves represent advantageous supports for preparation of heterogeneous catalysts due to large surface areas, high void volumes and narrow pore size distributions in mesopore area.

Four new heterogeneous metathesis catalysts **1** - **4** have been prepared by immobilization of commercial Grubbs 2nd and 3rd generation catalysts on the surface of mesoporous molecular sieve SBA-15 (S_{BET} = 829 m^2/g, V = 1.18 cm^3/g, d = 6.6 nm), modified with linkers bearing either dicyclohexylphosphine or pyridine end groups.



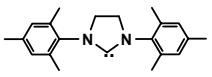
1

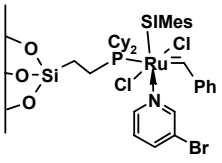


3

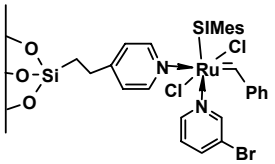
Cy = cyclohexyl

SIMes =





2



4

The catalysts exhibited a high activity and selectivity in ring closing metathesis (RCM) of diethyl diallylmalonate (DEDAM) as a model reaction (97 % conversion and 100 % selectivity for **2,** 30 min, 100 ^oC, Ru:DEDAM = 1:250). The catalyst **2** was also found very active in other types of metathesis reactions (homo- and cross metathesis, ring opening metathesis polymerization) of various substrates (unsaturated esters, terpenes). Filtration tests proved that the activity of the catalysts is bound to the solid phase. Catalyst **2** was successfully reused 6 times (RCM of DEDAM). It was found that catalysts **3** and **4** exhibited very low Ru leaching (only 0.18 % of the original content of Ru in catalyst, which represents 6.5 ppm and 3.7 ppm of Ru in the product for, **3** and **4**, respectively).

References:

Grubbs R.H., (Ed.), *Handbook of Metathesis*, Wiley-VCH, Weinheim, **2003**.

OXIDATION CHANGES PHYSICAL PROPERTIES OF PHOSPHOLIPID BILAYERS

Mgr. Lenka Beranová

Prof. Martin Hof

Oxidized lipids are generated from unsaturated glycerophospholipids under conditions of oxidative stress[1]. They influence the physical properties of biological membranes and also interact with specific receptors and affect signaling pathways. They are supposed to be involved in a range of human diseases. Therefore, they are extensively studied nowadays.

Physical properties of oxidized phospholipid (OxPL) membranes consisting of binary mixtures of 1-palmitoyl-2-oleoyl-sn-glycero-3-phosphocholine (POPC) and 10 % of one of two OxPLs - 1-palmitoyl-2-glutaryl-sn-glycero-3-phosphocholine (PGPC) or 1-palmitoyl-2-(5'-oxo-valeroyl)-sn-glycero-3-phosphocholine (POVPC), were investigated[2]. Fluorescence solvent relaxation (SR) and fluorescence correlation spectroscopy z-scan (FCS z-scan) show increased headgroup hydration and dynamics, and faster lateral diffusion in POPC membrane upon addition of OxPLs. The magnitudes of both effects are distinct for each of the two OxPLs.

Recently, we focused on different membrane compositions, we studied physical properties of membranes consisting of POPC, POPS and several types of oxidized phospholipids.

References:

[1] Fruhwirth, G. O.; Loidl, A.; Hermetter, A., *Biochim. Biophys. Acta* **2007**, *1772*, 718-736.

[2] Beranova, L.; Cwiklik, L.; Jurkiewicz, P.; Hof, M.; Jungwirth, P., *Langmuir* **2010**, *26*, 6140-6144.

HYDROTHERMAL SYNTHESIS OF SMALL PORE ZEOLITE AFX (SSZ-16)

Helena Dragounová

Ing. Pavel Hrabánek, Ph.D.
RNDr. Milan Kočiřík, CSc.

The aim of study was to develop and optimize current hydrothermal synthesis to prepare small pore zeolite AFX (SSZ-16) in a reproducible way. The crystallization of zeolite SSZ-16 was carried out under static and rotational conditions. In the case of static crystallization, highly pure SSZ-16 was only prepared at prolonged duration of crystallization. In order to decrease duration of crystallization, the microwave assisted synthesis was also performed using a special Teflon autoclave. However the product was amorphous according to XRD. Until now the crystals of zeolite SSZ-16 (confirmed by XRD) were only formed during hydrothermal synthesis at static conditions. If the crystallizations were performed at shorter time and/or with the addition of seeds then the samples contained substantial amount of the other zeolite phases (analcime, mordenite). The static hydrothermal synthesis procedure was further optimized particularly in the stage of ageing, temperature and duration of crystallization to maximize yield of pure SSZ-16. The crystals of SSZ-16 were characterized with SEM microscopy showing the agglomerated coffin-like crystals forming spherical core shells. The successful preparation of pure SSZ-16 was underlined by preservation of SSZ-16 structure after calcination performed at 550°C for 40 hours. Zeolite SSZ-16 with three-dimensional pore network (0.34×0.36 nm) is a promising candidate for highly important separation of CO_2 (0.33 nm) and CH_4 (0.38 nm).

FORMATION AND DECAY OF HNC/HCN IN THE POSITIVE COLUMN DISCHARGE

RNDr. Martin Ferus

Doc. RNDr. Svatopluk Civiš, CSc.

Molecules HCN and HNC have been studied in a positive column discharge using the time resolved continuous scanning FT spectroscopy in the spectral range 2000 - 6000 cm^{-1} with the resolution 0.05 cm^{-1}. Stable products in the exhaust were analyzed by the SIFT-MS spectrometry. Precursors BrCN, CH_3CN and $HCONH_2$ have been used for the study of the production mechanisms and decay processes of HCN/HNC ratio in the He or Ar glow discharge. Rotation - vibration bands of HCN and HNC have been observed in the ground and several excited states. The CN radical, N_2 and atomic lines of C, H, N have been presented in all measured spectra. In order to study the role of the hydrogen exchange in the reaction pathways deuterium has been applied.

HNC/HCN ratios from 3 % to 0.8 % were estimated using known transition dipole moments of the ground state v_1 bands. HNC/HCN ratio is influenced by the hydrogen partial pressure but it is not influenced by the precursor molecule. HNC/HCN chemical pathways were analyzed using kinetic model of the H-CN-HCN/HNC chemistry. Rate constant of the reaction

$$CN + H = HNC + H$$

was estimated to be 3.58×10^{-12} cm^3/molec.s at conditions of the He/Ar glow discharge and temperature 600 K.

MODIFIKACE POLOSENDVIČOVÝCH KOMPLEXŮ PRVKŮ 4B. SKUPINY ARYLAMINÁTOVÝMI LIGANDY

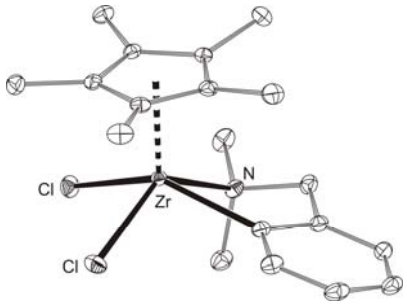
Ing. Aleš Havlík

Mgr. Michal Horáček Ph.D..

V oblasti organokovové chemie je vývoj nových či modifikace stávajících ligandů a jejich vzájemné kombinování neustále předmětem intenzivního studia. Pokud se zaměříme na sloučeniny přechodných kovů 4. skupiny (Ti, Zr, Hf), můžeme říci, že vedle aromatických cyklopentadienylových kruhů představují amidové a alkoxidové ligandy dva z nejčastěji používaných monodentátních aniontových ligandů.

Cílem této práce je příprava, charakterizace a studium vlastností organometalických sloučenin obsahujících aromatický cyklopentadienylový ligand v kombinaci s dalším C,N-chelátovým ligandem. C,N-chelatujícím ligandem je v prezentované práci N,N-dimethylbenzylamin, nesoucí elektron donorový atom dusíku. Sloučeniny podobného typu byly v literatuře popsány pouze pro atom titanu obsahující nesubstituovaný cyklopentadienylový[1] či spojený amido-cyklopentadienylový[2] ligand. N,N-dimethylbenzylamin v obou uvedených příkladech vystupuje jako bidentátní ligand vázaný ortho-atomem uhlíku k atomu kovu s dodatečnou koordinací atomu dusíku.

V rámci disertační práce byly dosud připraveny komplexy Ti, Zr a Hf obsahují penta- a tetra-methylovaný cyklopentadienylový ligand společně s a *N*,*N*-dimethylbenzylaminem. Takto substituované cyklopentadienylové kruhy byly zvoleny z důvodů potlačení nežádoucí reaktivity vysoce elektron deficitního kovového centra elektron-donačním efektem methylových skupin na cyklopentadienylovém ligandu. Jako výchozí sloučeniny byly připraveny polosendvičové trichloridové komplexy $(\eta^5\text{-}C_5Me_5)MCl_3$ a $(\eta^5\text{-}C_5HMe_4)MCl_3$ (M = Ti, Zr, Hf). Tyto komplexy reagují s jedním ekvivalentem 2-[(*N*,*N*-dimethylamino)methyl]fenyllithia za tvorby komplexních sloučenin $(\eta^5\text{-}C_5Me_5)MCl_2(C_6H_4CH_2NMe_2)$ a $(\eta^5\text{-}C_5HMe_4)MCl_2(C_6H_4CH_2NMe_2)$ (M = Ti, Zr, Hf). Získané nové komplexy Ti, Zr a Hf byly charakterizovány pomocí spektroskopických metod (NMR, IR, MS) ^1H a ^{13}C NMR spektra odhalila u všech komplexů teplotně závislé fluxionální chování v roztoku. Molekulová struktura v pevné fázi byla u většiny komplexů stanovena pomocí rentgenové difrakce.



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ELECTRODE COATING BY CHEMICAL MEDIATOR: THE AFM STUDY OF SURFACE NANOMORPHOLOGY

Mgr. Věra Hudská

Ing. Pavel Janda CSc.

Glassy carbon (GC) is still popular among electrode carbon materials due to its relative mechanical and chemical resistance and simple cleaning by polishing. The preparation of GC electrode mounted in Teflon includes polishing with emery paper and alumina, respectively, followed by ultrasonic cleaning in purified water before each experiment.

Subsequently, there are two, most frequent methods of surface modification:

1) Placing drop of solution containing studied compound on the GC surface [1]. Next step may include drying in air [2], drying under an infrared lamp [3] or in the oven [4].

2) Surface of the electrode is modified by electrodeposition from solution containing studied compound and the electrolyte. The deposition is carried out by applying repetitive potential sweeps at certain rate in specific potential range [5].

Scanning probe microscopy (SPM) techniques are successfully employed to characterize the structure of electrode surfaces [6]. In contrary to atomically flat basal plane of highly oriented pyrolytic graphite (HOPG) glassy carbon has rough and ill-defined surface. We present here an atomic force microscopy (AFM) study characterizing morphology changes upon modification of GC and HOPG electrodes, respectively. We demonstrate changes of GC and HOPG surfaces induced by chemical modification and influences of preparative procedure on GC surface morphology.

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STUDIES OF MOLECULAR SPECIES RELEVANT TO THE SAFETY ENGINEERING WITH AID OF SPECTROSCOPIC METHODS

Radmila Janečková

doc. Ing. Zdeněk Zelinger, CSc.
Dr. Laurent Margulés and Dr. Georges Wlodarczak

One of the principal and still open tasks of safety engineering concerns of the physical-chemical effects characterization related to the combustions, processes of matter burning and processes producing toxic species. The characteristic properties are connected with the chemical composition of the relevant processes - its components are as well intermediates and terminal products, which can be both reactive and stable particles.

More complete description of the microwave spectrum of formaldehyde in the excited vibrational states was performed in the region 150 – 660 GHz. The Cologne database involves only rotational spectrum within ground vibrational state for various isotopic species of H_2CO and this study will contribute to this database by new lists of rotational lines in the excited states ν_2, ν_3, ν_4 and ν_6 in the millimeter-wave and submillimeter-wave region. **[1]**

Gaseous n-pentylacetate (n-amylacetate) has been employed in dispersion studies instead of sarin. An extremely toxic nerve agent is represented by a non-toxic tracer with similar physical–chemical characteristics. The models for nerve agents, as tools of simulation, are very important for risk estimation and for safety and security research. The absorption spectra of gaseous $C_7H_{14}O_2$ were investigated by FT IR spectroscopy as well as CO_2-laser photoacoustic spectroscopy (PAS). CO_2-laser emission lines were used for photoacoustic detection of this molecule with detection limit in the range of 1–3 ppm. **[2]**

Latest section deals with studies of ions from the CN radicals family, radical cations XCN^+ (X = Br, I, Cl). The tunable infrared spectroscopy has been proved as an effective and sensitive method for detection of free radicals and molecular ions. Further as well the production modulation at hollow cathode discharge or microwave discharge has been proved as prospective in the spectroscopic research of radicals and ions inclusive carbon and nitrogen. The study of fundamental band of $BrCN^+$ has been performed by means of this method, however there was not performed the corresponding studies for ICN^+ a $ClCN^+$, that are our up-to-now non-successful target systems. These infrared spectra of studied ions are necessary precondition for possible subsequent research in the range of microwave spectroscopy. **[3]**

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CHARACTERIZATION OF AL SITING IN ZEOLITES USING ^{27}Al (MQ) MAS NMR. EFFECT OF COUNTER-CATIONS ON ^{27}Al OBSERVED AND ISOTROPIC CHEMICAL SHIFT

Ing. Petr Klein

Mgr. Jiří Dědeček, CSc.

In present time, zeolites (crystaline microporous alumino-silicates) are widely used in catalitic processes. One of key parameters which controls catalitic properities of Si rich zeolites is Al distribution in the zeolite framework, which can be determined using ^{27}Al MAS NMR [1,2]. Application of this approach to variety of zeolite types requires invariancy of NMR results to experimental conditions [3]. In this work, effect of various counter-cations (Li^+, Na^+, K^+, Rb^+, Cs^+, Mg^{2+}, Ca^{2+}, Ce^{3+}) on ^{27}Al observed and isotropic chemical shift of framework Al in different types of zeolites (chabazite with Si/Al ratio 2.7, zeolite Y with Si/Al 2.7 and zeolite A with Si/Al 1) was investigated. Each type of zeolite exhibits different dependence between chemical shift and type of balancing extra-framework cation. This effect does not reflect nuclear spin interactions and can be explained by the change of local Al geometry due to interaction of higher number of solvated cations in restricted space of channel system with the framework. In this case, the effect of counter-cation on the ^{27}Al shifts must be checked and suitable cation not affecting zeolite structure has to be used when ^{27}Al MAS NMR spectroscopy is applied to monitor Al distribution in the zeolite framework.

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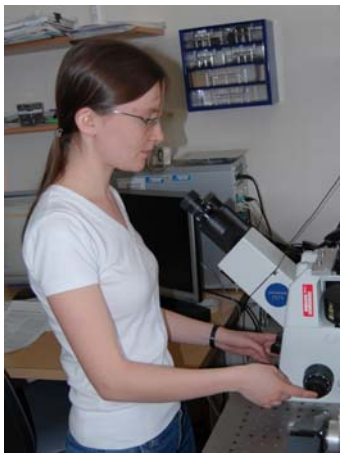

DYNAMICKÁ SATURAČNÍ OPTICKÁ MIKROSKOPIE POUŽÍVAJÍCÍ SVĚTLEM PŘEPÍNATELNÉ PROTEINY

Bc. Marie Kolářová

Mgr. Aleš Benda, Ph.D.

Fluorescenční mikroskopie je jednou z nejdůležitějších zobrazovacích metod používaných v biologii. Její význam spočívá ve vysoké citlivosti, kontrastu a v možnosti specifického označení sledovaných objektů. Limitujícím faktorem klasické fluorescenční mikroskopie je prostorové rozlišení, které je díky difrakci světla omezeno na max. 200 nm. Jednou z nových metod, které se snaží překonat difrakcí limitované rozlišení optického mikroskopu, je dynamická saturační optická mikroskopie[1] (DSOM). Zvýšeného rozlišení je dosaženo sledováním nelineární kinetiky dohasínaní fluorescenčního signálu při přechodu molekul ze svítivého do nesvítivého stavu. Pro praktické využití se jeví jako nejvýhodnější sledování přechodu do tripletového stavu fluoroforu[2] nebo přechodu do nezářivého stavu světlem přepínatelných fluorescenčních proteinů. Mezi přepínatelné proteiny se řadí Dronpa[3,4] a z ní odvozené varianty (rsFastLime, Padron, bsDronpa). Dronpu a její varianty lze opakovaně přepínat mezi fluorescenční a nefluorescenční formou pomocí blízkého UV (405 nm) a viditelného (488 nm) záření. Cílem mé diplomové práce je optimalizovat experimentální podmínky dynamické saturační optické mikroskopie využívající světlem přepínatelné proteiny a získat tak co nejvíce rozlišený obraz. Doposud byl na různých typech proteinů sledován vliv intenzity excitačního záření na rychlost dohasínání fluorescenčního signálu, fotostabilita proteinů a rychlost a mechanismus přepínání na různých časových škálách.

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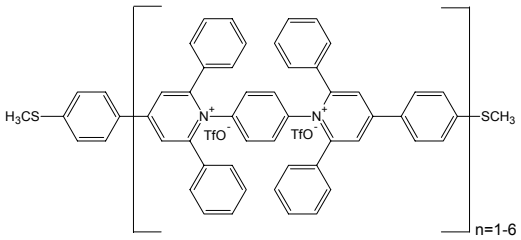
REDOX AND ELECTRONIC PROPERTIES OF MOLECULAR WIRES

Mgr. Viliam Kolivoška

Mgr. Magdaléna Hromadová, Ph.D.

Extended viologens are organic molecules designed for serving as molecular wires in the molecular electronic devices. Molecular wires are conducting objects with molecular-scaled radius and with the length that may exceed to macroscopic dimensions. Such wires should transfer electrons reversibly without spurious follow-up chemical processes (e.g. wire decomposition).



We study electrochemical and electronic properties of a series of molecular wires based on structures related to extended viologens. The wires consist of repeated units (from monomer to hexamer) terminated by alkyl groups (methyl, ethyl and *tert*-butyl) These groups show no significant effect on the behavior of wires.

We employ direct current (DC) polarography, cyclic voltammetry (CV), alternating current (AC) polarography and bulk electrolysis methods to study the nature of electron transfer in the molecular wires. Electrochemical impedance spectroscopy (EIS) is used to study the rate of electron transfer in the wires and in-situ spectroelectrochemistry (SEC) investigates the chemical stability of their various reduced forms.

With increasing numbers of repeating units in the molecule (n), the first redox potential shifts to more positive values, showing the limiting behavior. The shortest wire (n=1) accepts four electrons in four well discerned one-electron reversible steps. The dimer takes up two electrons in the first steps (10 in total). For n≥3, the wires accept reversibly 2n-2 electrons in the first step with no significant difference in the redox potential.

We use scanning tunelling microscopy (STM) to measure the single-molecule conductance of the wires. The deprotection of terminal alkyl groups was carried out in order to create thiol groups capable of chemisorption on the gold surface.

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SBĚR A ZPRACOVÁNÍ DAT A OVLÁDANÍ EXPERIMENTU POMOCÍ LABVIEW

Pavel Košťál

Mgr. Michal Fárník, Ph. D.

Klastr v našem pojetí je sdružení dvou (dimer) nebo více částic až po konglomeráty 10^3 a více molekul. Tyto klastry využíváme v naší laboratoři ke studiu elementárních procesů, jako je např. fotodisociace molekul. Klastr nám poskytuje prostředí v němž je molekula solvatovaná jako v makroskopickém prostředí a zároveň díky svým konečným rozměrům umožňuje výzkum daných procesů na molekulové úrovni. Studovanými systémy jsou např. atmosférické klastry, které sehrávají významnou roli při tvorbě ozónové díry, nebo klastry relevantní pro biofyziku.

K řízení, sběru a vyhodnocování dat nesmírně složitého a náročného experimentu byl vytvořen nový počítačový program založený na bázi programovacího prostředí LabVIEW. Program načítá data z osciloskopu, umí konvertovat časová spektra do hmotnostního spektra v případě, kdy se měří v modu s vysokým elektrickým polem. V případě měření v modu s nízkým elektrickým polem program převede časová spektra do spekter kinetických energií. Program umožňuje vstupní data zesílit, v případě nutnosti posunout v čase a ukládat jen část spekter pro další zpracování s důležitými daty v textovém formátu přijatelný pro další grafické programy, kteréžto jsou například Origin či Grace.

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Hans-Jochen Bartsch: Matematické vzorce (studentské vydání)

STUDIUM ADSORPČNÍCH VLASTNOSTÍ PESTICIDU ATRAZIN NA VYBRANÝCH PŘÍRODNÍCH MATERIÁLECH ZA POUŽITÍ POLAROGRAFICKÉ METODY

Jan Kříž***

Mgr. Magdaléna Hromadová, Ph. D.

Atrazin je herbicid triazinového typu, který zabraňuje fotosyntetickému procesu v zelených částech nežádoucích rostlin (plevelů). Byl zakázán Evropskou Unií v roce 2005, protože způsobuje kontaminaci spodních vod. Jeho zákaz souvisí s tím, že se splachuje vlivem dešťů do spodních vod a tudíž se nemůže rozkládat v povrchových vrstvách půdy vlivem světla jako jemu podobný Terbutylazin, který není zakázán.

Tato práce se zabývá adsorpcí Atrazinu na vybraných půdních vzorcích. V první části práce popisuji metodu pro určení výsledné adsorbce Atrazinu na vybrané materiály – tedy polarografii. V druhé části popisuji průběh celého pokusu od vytvoření kalibrační křivky, analýzu obsahu elektroaktivních látek ve vzorcích až po konečnou extrakci Atrazinu ze vzorků.

Výsledky pokusů ukázaly, že se Atrazin adsorbuje nejméně do polní půdy, což potvrdilo důvod jeho zákazu.

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INTERPRETATION AND MODELING OF TIME-RESOLVED IR SPECTRA

Mgr. Petr Kubelík

Doc. RNDr. Svatopluk Civiš, CSc.

Mathematical modeling of chemical reactions taking place in discharge plasma is a very important part of plasma research. Such modeling methods are commonly used in technological applications (for example: etching, deposition of thin layers, analytical spectroscopy etc.).

In our laboratory we are using glow discharge for production of radicals or ionic species. Developing of methods suitable for modeling of time-resolved IR emission spectra is necessary for comprehensive interpretation of obtained data.

Our spectra are measured with modified FT spectrometer with high spectral resolution. Maximal time resolution of this instrumentation is about 1 μs. This time scale is suitable for observing of most chemical reactions in glow discharge plasmas as well as many other molecular processes like quenching, vibrational relaxation etc.

There are many commonly used approaches for discharge modeling. These methods are usually focused on computing of parameters like electron density and concentration of charged particles based on knowledge of discharge current or voltage. Our goal is to implement methods suitable for estimation of concentrations of reactive species and their energy states during their formation and decay process. Results obtained from these models can be very useful for investigating and better understanding of chemical reactions and their mechanisms taking place before, during and after the discharge pulse.

SYNTHESIS AND PROPERTIES OF NOVEL TNU-9, IM-5 AND SSZ-74 ZEOLITES

Ing. Martin Kubů

Prof. Ing. Jiří Čejka, DrSc.

Zeolites, microporous aluminosilicates with crystalline structure, are widely used in catalysis, adsorption and separation due to their shape selectivity properties, acidity and high surface areas [1]. According to the Structure Commission of the International Zeolite Association (IZA) approximately 200 different framework types are known.

My work focuses on the synthesis, characterization and modification of novel TNU-9 [2], IM-5 [3] and SSZ-74 [4] zeolites with the most complex structures known [5]. These zeolites are closely related to the most frequently used
ZSM-5 zeolite having three-dimensional 10-ring channel system. Zeolites were synthesized hydrothermally with diquaternary alkyl ammonium ions based on N-methyl pyrrolidine as organic structure-directing agents (SDAs) differing only in the length of the carbon chain between two heterocyclic rings.

Following effects were investigated. Different aluminum sources, crystallization time, incorporation of more aluminum into the SSZ-74 framework and incorporation of gallium and germanium instead of aluminum into the framework of TNU-9 zeolite. X-ray powder diffraction, scanning electron microscopy, nitrogen sorption isotherms and FTIR spectroscopy to evaluate the acidic properties were used for characterization of prepared materials. H-forms of TNU-9, IM-5 and SSZ-74 were tested in toluene alkylation with isopropyl alcohol and disproportionation of toluene. Based on catalytic results, their structures seem to be more opened when compared with ZSM-5 and ZSM-11 providing higher conversions and interesting selectivities to primary alkylation and disproportionation products.

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ELECTROCHEMICAL REDUCTION OF MOLECULES WITH MORE REDOX CENTERS: MONO-, DI-, TRI- AND TETRANITROCALIX-[4]-ARENES AND THEIR MODELS

Alan Liška

doc. RNDr. Jiří Ludvík, CSc.

Calixarene is a stable supramolecular frame able to bear various substituents – redox centers or ligands, capable to exhibit unusual redox properties including host-guest interaction. For these reasons a suitable substitution is necessary, namely on the upper rim. The title nitro derivatives are precursors enabling electrochemical introduction of other functional groups and prolongation of the pendant carbon chains.

These poly-nitro compounds are also an example of molecules with more redox centers. The presence of one, two, three or four nitro groups in one molecule provokes many principal questions: What is the intramolecular electronic interaction between them? Are they reduced simultaneously or stepwisely? Which part of the molecule is reduced first? What is the role of the lower rim substitution in the reduction of the nitro groups? What is the influence of the conformation of the calix arene (CONE, PACO, 1,2-ALT, 1,3-ALT) on its reducibility? What is the influence of the reduction on the molecular geometry?

At first, the reduction mechanisms of p-subatituted nitrobenzenes in aprotic DMF had to be clear. Besides the classical nitro group reduction (1rev. + 3 electrons), several other mechanisms (dianion formation, 6-electron reduction, dimerization, autoprotonation mechanism, etc.) depending on *p*-substitution were observed and described.

Electrochemical reduction of the tetranitrocalix-[4]-arenes starts with two 2-electron reversible waves corresponding to the presence of two different couples of equivalent non-communicating nitro groups. This result reflects well the finding of the x-ray structural analysis, that the "calix" has in fact a pinched shape with a strong "π-stacking" of the opposite benzene rings. The first two waves are followed by a single 12-electron wave.

The quantum chemical calculations (electrostatic potential maps of the neutral molecule as well as of the mono-, di-, tri- and tetraanion and localization of HOMO and LUMO of the dianion) confirmed the above mentioned interpretation of experimental data and revealed, that the first electron transfers attacks the "distant" nitro groups, whereas the pinched position is reduced at more negative potential.

The electrochemical results of a series of mono-, di-, tri- and tetranitrocalixarenes are fully consistent with previously described type of redox behaviour.

In addition to this, the role of the lower ring substitution and conformation type of the calixarenes are discussed.

Acknowledgement: *The author thanks to prof. Pavel Vojtisek (Charles Univ., Prague) and to prof. Pavel Lhotak (Prague Inst. of Chem. Technol.) for granting the compounds and to prof. Albert Fry (Wesleyan Univ., CT, USA) for the computation. The financial support of the project KONTAKT No. ME 00209 (Ministry of Education, Youth and Sports of the Czech Republic) is highly appreciated.*

A NOVEL ANTIMICROBIAL PEPTIDE ARENICIN-1 AND ITS LIPID-SPECIFIC INTERACTION WITH MODEL MEMBRANES

Mgr. Radek Macháň

Prof. Martin Hof, DSc.

Arenicin-1 is a novel antimicrobial peptide from the marine lugworm *Arenicola marina*. It has unique secondary structure of a β-hairpin stabilized by a disulphide bond (Ovchinnikova et al.). It is effecting against most bacterial strains and toxic for some eukaryotic cells but not haemolytic (Andrä et al.). The specificity of antimicrobial peptides against prokaryotic cells is usually related to different electrostatic charge of outer leaflet of plasma membrane of prokaryotes (contains anionic lipids) and eukaryotes (purely zwitterionic lipids).

Laser scanning microscopy (LSM) and *Z*-scan fluorescence correlation spectroscopy (FCS) were employed to characterize the interaction mechanism between arenicin-1 and supported lipid bilayers (SLBs) of 3 different lipid compositions. Those were purely zwitterionic lipids (DOPC), a mixture of zwitterionic and ionic lipids (DOPC/DOPS 4/1) and a bilayer with phase separation of lipids (DOPC in liquid crystalline phase and DSPC in gel phase). Lipids labelled with Bodipy FL (excited by 470 nm laser) were added to the SLBs and fluorescently labelled peptide analogue arenicin-1-Atto655 (excited by 640 nm laser) was used for visualization of peptide by LSM.

Arenicin-1 was found to form immobile structures on the SLBs of all compositions. There exists however a significant difference in the way how immobile arenici-1 structures influence the lateral mobility of lipids in SLBs. While their mobility in zwitterionic SLBs is insensitive to arenicin-1 structures, a significant decrease of lipid lateral diffusion coefficient at arenicin-1 concentrations exceeding 1μM was observed in SLBs containing anionic lipids. *Z*-scan FCS diffusion law analysis (done according to Humpolíčková et al.) indicates presence of microdomains. We explain their appearance by crosslinking of anionic lipids by arenicin-1 structures. LSM also showed that in SLBs containing gel and liquid crystalline phase arenicin-1 binds preferentially to areas of phase boundary.

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SUPERSONIC DISCHARGE RADICAL SOURCE: NOZZLE GEOMETRY INFLUENCE ON THE OH RADICAL GENERATION

Mgr. Milan Mašát

Mgr. Ondřej Votava PhD.

In our research we focus on the spectroscopy of molecular radicals, highly reactive species which play important role in broad range of chemical reactions in atmosphere. Due to their high reactivity, molecular radicals have to be generated and studied in-situ. In our experiment radicals are produced by stable precursor dissociation in an electric discharge followed by a supersonic expansion into vacuum. In such experiment molecular beam with a high concentration of internally cooled molecular radicals is produced. High resolution overtone spectroscopy is used to probe the produced radicals.

Similar radical sources have been used by several researchers in the past. Although it is well known that the discharge properties depend quite significantly on the geometry of the discharge region, we are not aware of any systematic research of the relation between production of molecular radicals and the radical source geometry. As long as a sufficient concentration of radicals is reached the source is commonly not altered. We have however discovered that easily implemented modifications in the geometry can dramatically change radical concentrations and properties.

In this contribution we present three basic geometries of our radical source. Change in molecular radical concentrations and other important features, such as their temperature are presented for those three geometries.

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POLOSENDVIČOVÉ TITANIČITÉ KOMPLEXY OBSAHUJÍCÍ VAZBU KŘEMÍK-VODÍK

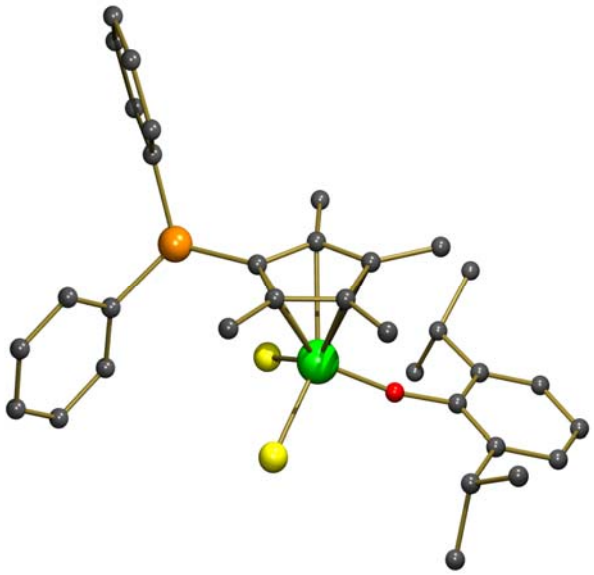
Václav Oborník***

Mgr. Michal Horáček, Ph.D.

Prezentovaná práce se zabývá přípravou nových křemíkem substituovaných cyklopentadienylových ligandů a syntézou odpovídajících polosendvičových titaničitých komplexů.

Za tímto účelem byla na cyklopentadienylový kruh zavedena dimethylsilanová nebo difenylsilanová skupina obsahující reaktivní vazbu křemík-vodík. Takto modifikovaný cyklopentadienylový ligand byl navázán na titanový atom transmetalační reakcí lithné soli cyklopentadienu s chloro-tris(isopropoxo)titaničitým komplexem. Vzniklé polosendvičové titaničité komplexy, obsahující tři isopropoxo ligandy, byly pomocí dichlordimethylsilanu převedeny na trichloridová analoga.[1]

Připravené monocyklopentadienyltrichlorotitaničité komplexy byly dále modifikovány záměnou jednoho chloridového atomu za 2,6-diisopropylfenolátový či (2,6-diisopropylfenyl)amidový ligand. Důvodem pro tuto záměnu je využití odlišných elektronických (zavedení heteroatomu) i sterických vlastností těchto ligandů pro ovlivnění reaktivity centrálního atomu titanu.



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PROTEIN RADIATION CHEMISTRY: FROM AMINO ACIDS PHOTOSTABILITY TO DAMAGE OF TERTIARY STRUCTURE

Ing. Milan Ončák

Doc. RNDr. Petr Slavíček, Ph.D.
Mgr. Michal Fárník, Ph.D.

This contribution is focused on the stability of aminoacids and proteins with respect to the radiation, i.e. photoexcitation and photoionization. Photostability represents a key aspect in several fields, such as radiation damage of biomolecules, origin of life on Earth or X-ray crystallography. It was found that amino acids themselves show surprising photostability and they are even able to sustain space UV radiation, as they were found in e.g. the Murchinson meteorite.[1]

In the first part, I shall concentrate on the photochemistry of the simplest amino acid, glycine.[2] I will show that microsolvated glycine zwitterion is not stable towards electronic excitation, with C-N bond dissociation as the main photochemical channel. On the other hand, when the glycine zwitterion is embedded by water solvent molecules, the electronic excitation quickly dissipates and transforms into heat. Glycine thus gains photostability via solvation. This is in a full agreement with experimental findings where glycine was found to be photostable in the ice clusters.

In the second part, I will present some insights into radiation damage of the tertiary protein structure. I will focus on the recently discovered new type of link bond in collagen IV, the sulfilimine bond -N=S-.[3] First, it will be argued that in the protein, the sulfilimine bond exists most likely in a protonated form. As such, the -N=S- bond is stable towards both excitation and ionization. However, it is not prone to the electron attachment and readily dissociates. We may thus rationalize the experimental observation of -N=S- bond rupture under X-ray by dissociative electron attachment process in reaction with solvated electron produced by ionizing radiation. Finally, comparison to the experimentally well investigated properties of the disulfide link bond will be provided.

To study the radiation damage induced on the proteins, we have employed various tools of theoretical chemistry, including single- and multireference *ab initio* calculations, semiclassical *ab initio* molecular dynamics or absorption spectra calculations based on the reflection principle. To estimate the reaction rate constants of the dissociative electron transfer processes, we have employed modified Marcus theory.

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INVESTIGATION OF MATTER TRANSPORT IN POROUS MATERIALS BY MEANS OF PFG NMR

Bc. Mikuláš Peksa

RNDr. Milan Kočiřík, CSc.

Measurement of liquid self-diffusion inside pore system using NMR appears to be a powerful method to determinate geometrical characteristics of porous materials. The main idea of this approach is based on the fact that diffusion in pores is restricted by pore boundaries. Geometrical characteristics of pore system can be evaluated from comparison of the mean square displacement of a tracer molecule in porous system with that in free liquid. NMR is an ideal tool for this type of measurement because it is capable to measure movement restrictions on both short and long length scale. But the measurement protocol has to be adjusted for each single type of porous material. We have optimized the conditions for glass beads pack.

Our samples of glass spheres were put in NMR tubes and then immersed in n-hexane. Pulse sequence which we used was based on stimulated echo in order to suppress influence of transversal relaxation. This pulse sequence allowed us to vary the diffusion time between 10 ms and 2 s. Our measurements were carried out at room temperature and the mean square displacement of the tracer molecule was in range of about 40 to 8 000 μm^2. Doubled pulse sequence was used in order to eliminate influence of possible convection on measurement. The evaluated geometrical characteristics of the system were surface-to-volume ratio of the pore system and the tortuosity.

The measurements showed a considerable effect of particles arrangement in the sample on its geometrical characteristics. The tortuosity and porosity of the sample increased as the width of particle size distribution increased.

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ANALYSIS OF IODOMETHYL RADICAL, $CH_2I\cdot$ ($\tilde{X}^2B_1$)

Ing. Jan Skřínský[1,2]

doc. Ing. Zdeněk Zelinger, CSc[1],
Dr. Stephane Bailleux[2]
prof. Georges Wlodarczak[2]

$CH_2I\cdot$ radical is a member of halogen substituted methyl radicals denoted CH_nX_{3-n}, where n = 0−2 and X = F, Cl, Br, and I. These radicals change their molecular structure from planar to non-planar on increasing halogen atoms number. The reason for such behavior could be investigated from the molecular and electronic structure of $CH_2X\cdot$ radicals, where X = F, Cl, and Br as well-studied halogen analogues of $CH_2I\cdot$ [1].

In addition to its importance in molecular spectroscopy is this radical also related to the possible extensive iodine-mediated atmospheric ozone destruction [2] as well as methane flame inhibition by halogenated hydrocarbon chemical extinguishment [3].

Millimeter-wave spectra of the $CH_2I\cdot$ radical have been observed in the ground vibronic state in the frequency range 200−610 GHz. More than 1000 *a*-type transitions that span the values $12 \le N' \le 35$ and $K_a \le 6$ were analyzed with the experimental accuracy better than 50 kHz. A global least-squares analysis of the measured lines was conducted and led to the determination of rotational, centrifugal distortion, fine and hyperfine molecular constants. This allowed a systematic comparison of the structural and bonding properties among the $CH_2X\cdot$ analogues (where X = F, Cl, Br, and I) based on fine and hyperfine coupling constants (*A* Reduction, I^r Representation) [4].

The present analysis of gas phase investigation has completed the series of studies by high-resolution rotational spectroscopy of the monohalogen-substituted methyl radicals. The investigation of production by-product ICl is in progress. Measurements of the vibrational emission and absorption transitions in the infrared region could be conducted in the near future with the high resolution infrared experimental apparatus from J. Heyrovský Institute of Physical Chemistry.

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[1] Department of Photochemistry, Spectroscopy and Ion Chemistry, J. Heyrovský Institute of Physical Chemistry.
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FEMTOSECOND NON-ADIABATIC MOLECULAR DYNAMICS: A STUDY OF PHOTOCHEMICAL DEACTIVATION OF INDOLE MOLECULE

Ing. Lukáš Sobek

Mgr. Jiří Pittner Dr. rer. nat.

Photochemical behaviour of indole can be explained by the presence of polarity dependent channel of radiationless deactivation attributable to hydrogen predissociation from NH bond in non-polar non-hydrogen bonding solvents and photoinization in water as presented in [1]. Our goal is performing the simulation of deexcitation process with the quasi-classical molecular dynamics (MD) in which non-adiabatic transitions are computed in Tully's fewest switch surface hopping algorithm [2].

We employed state-averaged complete active space self-consistent field method (SA-CASSCF) using standard split-valence double zeta Gaussian basis set 6-31 G with polarization functions on carbon atoms and on hydrogen atom of the NH group. Correct description of σ^* orbital located near NH bond needed s- and p-diffuse functions (exponent 0.0639) located on nitrogen atom and s-diffuse function (exponent 0.036) centered on adjacent hydrogen atom. The active space involved 10 electrons in 8 orbitals. Four lowest quantum states of indole, i.e. S_0, S_1 (L_a), S_2 (L_b) (both of $\pi\pi^*$ character) and S_3 ($\sigma\pi^*$) were treated with weight 0.25 in the state-averaging procedure.

Potential energy profiles along the NH-bond stretch were computed by means of coordinate-driven minimum-energy-path approach: for a given value of bond distance all remaining intramolecular coordinates were optimized with CASSCF analytical gradient. Initial conditions for the MD simulation were sampled using a Wigner distribution for temperature 300 K, starting from S_2 state (excitation UVc computed wavelength 250 nm). Total 69 trajectories were run for 500 fs each. We performed exponential fitting of the S_2-state-depopulation curve and obtained the half-time of depopulation to be 11.9 fs.

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SELECTED ION FLOW TUBE MASS SPECTROMETRY (SIFT-MS):

FUMES OF EXPLOSIVES AND PLANT ODOURS

Mgr. Kristýna Sovová

RNDr. Patrik Španěl Dr. rer. nat.

Selected ion flow tube mass spectrometry is a technique for accurate quantification of trace amounts of gases including vapours of volatile organic compounds present in ambient humid air. This technique was mainly used for analyses of compounds present in human breath. However, it has a potential to be used in other areas of interdisciplinary research including forensic science and also plant physiology with the ultimate aims of mechanisms involved in use of plants for decontamination of polluted soil. The initial results in these areas are presented.

In order to study degradation products of explosives material SIFT-MS technique was coupled together with Laser Induced Breakdown Spectroscopy (LIBS). Thus a small amount of a sample was irradiated by ArF laser and stable gaseous products were analyzed simultaneously using SIFT-MS. More than forty types of explosives were studied in this experimental set-up and a spectral database was obtained.

As a prelude to plant physiology studies, we have investigated essential ion chemistry involving plant odour compounds. Plants release these volatiles to atmosphere during their growth and development. They play a role in communication between species and also as a defence against herbivores. The aim of this study was to obtain the rate coefficients and to determine the product ions of the ion-molecule reactions. This data will be necessary for identification and real time quantification during the anticipated measurements of plant odours.

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FLUORESCENCE CROSS-CORRELATION SPECTROSCOPY AS A TOOL FOR STUDY OF INTERACTION BETWEEN THE UNILAMELLAR VESICLES AND THE PEPTIDES

Ing. Tomáš Steinberger

prof. Martin Hof, DSc.

Fluorescence cross-correlation spectroscopy (FCCS) is a method based on ideas of fluorescence correlation spectroscopy (FCS) which monitors the fluorescence intensity fluctuations of single labeled molecules moving in and out of a confined illuminated volume. Interpretation of FCS data is based on a statistical autocorrelation analysis of the time scale of fluctuations.

By contrast, FCCS measures the temporal fluorescence fluctuations coming from two differently labeled molecules diffusing through a small sample volume. Afterwards, the measured fluctuations are evaluated by cross-correlation analysis of the fluorescence signals from separate detection channels. By this way the information of the dynamics of the dual-labeled molecules is extracted. FCCS is used as a tool for the characterization of diffusion coefficients, binding constants, kinetic rates of binding, and determining molecular interactions in solutions and cells.

At first we used FCCS to measure double labeled large unilamellar vesicles (LUV), there should be highest achievable positive correlation. The second step was measurement with a mixture of vesicles which are labeled with two dyes but every vesicle only by one type of the dye. There should not be cross-correlation, because they move independently of each other. If there is some cross-correlation, it means that there is imperfect separation of fluorescence from the two dyes. In the third step we used mixture of two differently labeled vesicles with vesicles which were labeled with both dyes.

In the last series of experiment we tried to measure vesicles which were labeled with one dye and has the other type of dye in inside solution. After interaction between this vesicles with membrane active peptides, there should be measured some leakage of inside dyes induced by pore forming peptide.

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LASEROVÁ FOTOAKUSTICKÁ SPEKTROSKOPIE V KONDENZOVANÉ FÁZI

Bc. Jan Suchánek

doc. Ing. Zdeněk Zelinger, CSc.

Práce se zabývá vývojem laserové fotoakustické spektroskopie v kondenzovaném stavu. Tato metoda je založena na fotoakustickém jevu – tedy generování akustického signálu ve vzorku po interakci s elektromagnetickým zářením v důsledku nezářivé relaxace energie. Tento signál lze snímat a dále vyhodnocovat pro získání analytických informací. Metoda se často používá jako doplňková metoda k zavedeným optickým metodám při studiích interakce elektromagnetického záření s látkou a poskytuje energetické a kinetické informace o excitovaných speciích. Výhodou oproti optickým metodám je možnost provádět měření v opticky nečistých vzorcích. Hlavním cílem je sestavení a zprovoznění měřící soustavy a její optimalizace pro sběr a získávání experimentálních dat. Jsou provedena pilotní měření s látkami poryfyrinového typu, které jsou běžně touto metodou studovány, a dále měření s nově syntetizovanou látkou – boranovým komplexem.

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METAL ORGANIC FRAMEWORKS IN ORGANIC SYNTHESIS

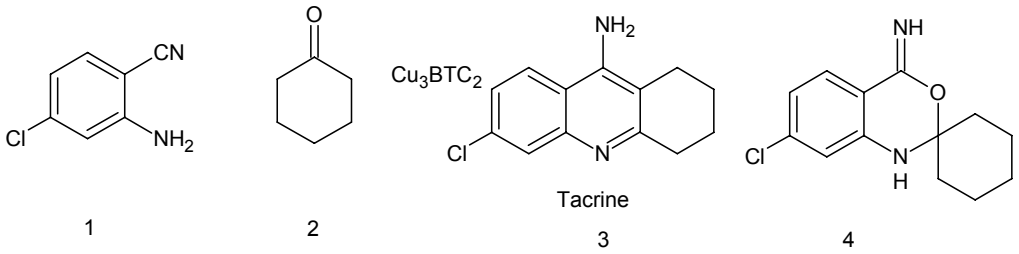
Mgr Katarzyna Sulisz

Prof. Ing.. Jiří Čejka, DrSc.

Metal Organic Frameworks (MOFs) are a class of materials useful for gas storage, gas purification and separation applications with a great potential for industrial use. They are also a very promising group of materials for heterogeneous catalytic purposes due to their well ordered structures, high surface areas, and lack of non-accessible bulk volume [1].

My PhD thesis is focused on the application of Metal Organic Frameworks in various reactions (Friedländer, Knoevenagel) leading to significant pharmaceutical compounds.

The catalytic activity of [$Cu_3(BTC)_2$ – Basolite C300, Sigma-Aldrich] Metal Organic Framework was tested in the reaction between aminonitriles (1) and different cyclic and aliphatic ketones like cyclohexanone (2), cyclopentanone or acetylacetone.



Scheme1. Friedländer annulation catalyzed by Cu_2BTC_3 yielding Tacrine.

In the case of reaction between chloroaminonitrile (1) and cyclohexanone (2) the reaction was completed in 5h, yielding Tacrine (3) in 49 % and its analogue (4) in 51% in solvent-free conditions (Scheme 1). Cu_3BTC_2 is the most efficient catalyst for the Friedländer reaction in comparison with molecular sieves presenting Lewis acid character like H-BEA or (Al)SBA-15.

Further study will be centered on the application of MOFs in the synthesis of 1,5 – benzodiazepine derivatives [3] and Knoevenagel condensation between acetylacetone and benzophenone or benzaldehyde. Also other MOF structures will be tested for their catalytic possible use.

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KONSTRUKCE A CHARAKTERIZACE DIODOVÝCH LASERŮ PRO ANALÝZU STOPOVÝCH MNOŽSTVÍ LÁTEK V PLYNNÝCH VZORCÍCH

Vít Svoboda***

Mgr. Ondřej Votava, Ph.D.

Spektroskopie patří mezi analytické metody, které se používají při studiu procesů probíhajících v atmosféře. Výhoda spektroskopie oproti jiným metodám spočívá např: ve vysoké citlivosti, specificitě a možnosti měření na dálku. Podmínkou pro přesná spektroskopická měření je kvalitní zdroj záření. V poslední době se ukazují jako velice užitečné zdroje záření laserové diody.

Avšak i v rámci jedné výrobní série se mohou charakteristiky diod více či méně lišit. Pro jejich úspěšné nasazení ve spektroskopickém experimentu potřebujeme tyto charakteristiky detailně znát, jelikož jinak nejsme schopni používat diodu efektivně a zabránit jejímu poškození.

V rámci práce bylo mým úkolem navrhnout experimentální sestavu, ve které bude možno tyto charakteristiky změřit. Následovně charakteristiky zpracovat a vytvořit ke každé diodě, která se v laboratoři používá, průvodní list, ve kterém budou charakteristiky zaneseny. Celá moje práce má sloužit jako prostředek umožňující práci s těmito diodami a přinese i možnost jejich budoucí diagnostiky - zjištění případného poškození. To se bude provádět porovnáním s mými výsledky, jelikož všechny charakteristiky se poškozením diody mění.

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DECOMPOSITION MECHANISM OF 1,1-DIAMINE-2,2-DINITROETHENE (FOX-7) A SPECTROMETRIC STUDY

Mgr. Ludmila Šimková

Doc. RNDr. Jiří Ludvík, CSc.

Recently synthesized compound 1,1-diamine-2,2-dinitroethene[1] (FOX-7), is an energetic material with low sensitivity and high performance. Due to two nitrogroups and a double bond, the molecule is easily reducible. In addition to this, the presence of two geminal aminogroups creates a so called push-pull effect of electrons. In other words, one part of the molecule is strong oxidation center and the opposite part is an electron donor. Therefore the electron structure of this species is unbalanced enabling intramolecular electron transfer reactions. The main goal of this project is to understand the reaction abilities of this complicated system with multiple redox centers.

Whereas under analytical conditions (small electrode, large volume and low concentration) the reduction process involves expected 18 electrons, the exhaustive electrolysis even in acidic media shows the consumption of only 6–7 electrons per a molecule. Moreover, after the electrolysis no expected organic product (1,2-diaminoethan) was detected, only gases were found and identified. This finding suggests the analogy of the observed reduction-initiated degradation reaction with the chemical process during explosion. For understanding the mechanism the interception of intermediates is necessary. For this purpose we used the following spectrometric techniques.

At first, CID (collision-induced dissociation) technique in mass spectrometry was utilized. This approach can simulate degradation of FOX-7 by electrical impulse which results in bond breakage and the fragmentation of the molecular ion into smaller fragments analyzed by a mass spectrometer.

Other methods which can help us to understand the process of degradation of FOX-7 are LIBS and SIFT-MS. These techniques allow to study in laboratory environment short-living species and molecules formed during explosion.

In addition to this, during electrolytic reduction of FOX-7 (namely in aprotic media) changes of color are observed. For this purpose an UV/Vis spectrometric study was performed. Since the parent molecule can exhibit tautomeric changes depending on the media, first part of experiments (still without electrolysis) involves a concentration and pH-dependence of spectra together with measurements in various organic solvents. The next task was spectroelectrochemical investigation of FOX-7 during electrolysis with attempts of identification of intermediates and products.

Acknowledgement: The support of the grant IAA400400813 (GAAVČR) is appreciated.

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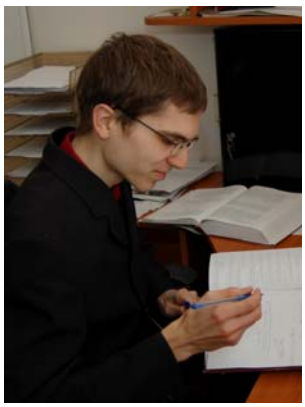

ROTATIONAL EXCITATIONS OF POLAR MOLECULES BY COLD ELECTRONS

Mgr. Miroslav Šulc

Mgr. Roman Čurík, Ph.D.

Collisions of cold electrons (with incident energy of order of a few tens of meV) with molecules play a rather dominat role in a diverse range of scientific and technological fields of interest. Among these are mainly astrophysics, physics of planetary atmospheres, energy related technologies such as issues concerning carbon dioxide lasers or material damage in fusion powered reactors etc. [1, 2].

The theoretical description of the underlying physical processes is complicated by the inherent many-body character of the scattering system. Extending the approach outlined in [3, 4], we present a few-parametrical model tailored to description of rotational excitations of gaseous molecules. Our approach is based on combination of the frame transformation theory [5] and rigid rotor approximation. The free parameters (related physically to the well-known concept of phase shifts in case of scattering in spherically symmetric fields) are fitted to the experimental data [6]. Exploiting this framework enables us consequently to extract individual rotational state-to-state cross sections. These data acquired by the joint collaboration of the experimental and theoretical techniques are inaccessible by direct measurements. Therefore our state-to-state cross-sections belong to very few sources available for cold energy applications mentioned above.

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A STUDY OF CALIXARENE SELF-ASSEMBLED MONOLAYERS ON GOLD METAL SURFACES

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Self-assembly process is one of the useful tools of the electrode surface modification. The main aim of this process is directed toward creating well defined, sufficiently stable and reproducible model systems, permitting electrochemical measurements on the basis of which it is possible to lower the detection limits and improve the selectivity of electrodes to specific ions or molecules.

In our laboratory, –SH substituted synthetic macrocyclic molecules of calixarenes, which are covalently bonded to the gold electrode surface via these thiol groups with formation of compact monolayers, are used to change the electrochemical properties, compared to bare gold electrodes. The main aim of our work is the utilization of calixarenes as ligand molecules in designing an ion-selective sensor, based on monitoring of differences in the properties of the electric double layer in the presence of different ions.

The first results on the calixarene self-assembled monolayer (SAM) structure and the conditions of SAM formation on gold surfaces were discussed in our previous work. Now we are studying the electrochemical behavior of the calixarene modified gold electrode in various electrolytes.

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MULTIFREQUENCY – DOMAIN LIFETIME DATA ANALYSIS USING PHASOR PLOT APPROACH

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The phasor method of treating fluorescence lifetime data first introduced by Jameson et al. provides a facile and convenient approach to characterize lifetime heterogeneity and to detect the presence of excited state reactions, such as solvent relaxation. Up to the present day phasor approach has been successfully introduced into fluorescence lifetime imaging microscopy (FLIM), where lifetime analysis in each pixel might be very complicated because of low fluorescence signal. The phasor method utilizes a plot of M sin(Φ) versus M cos(Φ), where M is the modulation ratio and Φ is the phase angle taken from frequency domain fluorometry. A principle advantage of the phasor method is that it provides a model-less approach to time-resolved data, amenable to visual inspection. The use of phasors is not limited to frequency domain data, as time domain data may also be used to construct phasor plots.

In my study, the phasor method is used to investigate binary and ternary mixtures of single-exponential fluorescent dyes, as well as dipolar relaxation in a homogeneous solvent, in vesicles and within the heme binding pocket of two types of apomyoglobins.

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QUANTUM COMPUTING APPLIED TO CALCULATIONS OF MOLECULAR ENERGIES: CH_2 BENCHMARK

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Quantum computers are appealing for their ability to solve some tasks much faster than their classical counterparts. To be more precise, there exist polynomially scaling algorithms to solve tasks, for which only algorithms with an exponential scaling on conventional computers are known. The most prominent example is the famous Shor's algorithm for factoring integers, with potentially far-reaching consequences for cryptography.

For quantum physics, the Abrams's and Lloyd's polynomially scaling algorithm for solving the many-body Hamiltonian eigenvalue problem [1] is of central importance. Its use in quantum chemistry was first proposed in [2]. It was shown that quantum computers, if available, would be able to perform the full conguration interaction (FCI) energy calculations with a polynomial scaling. This is in contrast to conventional computers where FCI scales exponentially.

We have developed the code for simulation of a quantum computer and imple- mented our version of the quantum full conguration interaction (QFCI) algorithm using iterative phase estimation [3]. In this approach, only one ancillary qubit in the read-out part of the quantum register is needed. We will present a detailed description of this algorithm and the results of the tests of its performance on the four lowest lying electronic states of methylene molecule (CH_2). This molecule was chosen as a benchmark, because both of the lowest lying $^1A_1$ states exhibit multireference character at the equilibrium geometry.

It has been shown that with a suitably chosen initial state of the quantum register one is able to achieve the probability amplication regime of the iterative phase estimation even in this case.

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