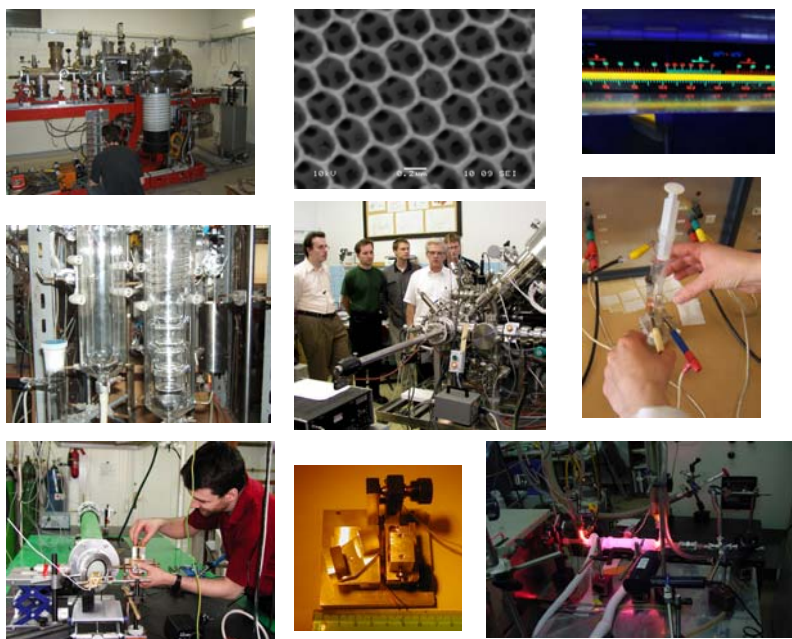


Ústav fyzikální chemie Jaroslava Heyrovského AV ČR



# Seminář studentů ÚFCH JH

13. -14. června 2006

Praha



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# Seminář studentů ÚFCH JH

Praha, 13.-14.6.2006

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Doc. Martin Hof, Dr. rer. nat.



**Úterý 13.6.2006 (dopoledne)**

Čas	Předsedající	Přednášející	Název
<b>8:15</b>	<b>Zahájení semináře studentů</b>		
8:20	<u>Tereza KOSTLÁNOVÁ</u>	Jan DEMEL ( <i>I.ročník</i> )	PALLADIUM NANOPARTICLES GRAFTED ONTO MESOPOROUS MOLECULAR SIEVE MCM-41
8:40		Anna ZANĚ ( <i>I.ročník</i> )	THE SPBS VERSUS GUVS – THE FINAL COUNTDOWN
9:00		Eva GRIGOROVÁ ( <i>diplomantka</i> )	ODHAD DISTRIBUCE TĚŽKÉHO ATMOSFÉ- RICKÉHO POLUTANTU V MĚSTSKÉ AGLOME- RACI S VYUŽITÍM CO <sub>2</sub> – LASEROVÉ OPTO- AKUSTICKÉ METODY V NÍZKORYCHLOSTNÍM AERODYNAMICKÉM TUNELU
9:20		Jiří BRABEC ( <i>I.ročník</i> )	AUTOMATICKÉ GENEROVÁNÍ KÓDU MULTI- REFERENČNÍ BRILLOUIN – WIGNER METODY VÁZANÝCH KLASTRŮ – TENSOR CONTRACTION ENGINE
9:40		Barbara GASIŇSKA ( <i>I.ročník</i> )	DNA CONDENSATION INFLUENCED BY COUNTERIONS –FLUORESCENT CORRELATION SPECTROSCOPY APPLICATIONS
<b>10:00</b>	<b>COFFEE BREAK</b>		
10:10	<u>Jan ŠMYDKE</u>	Vladimír NAVARA ( <i>diplomant</i> )	THE EFFECT OF SUPPORT ON THE SEPARATION PROPERTIES OF MEMBRANE
10:30		Justyna BARUCHA ( <i>I.ročník</i> )	THE INFLUENCE OF THE PRESENCE OF IONS ON THE WATER ORGANISATION IN THE HEADGROUP REGION OF LIPID BILAYERS: A SOLVENT RELAXATION STUDY
10:50		Jiří OLŠÁK ( <i>diplomant</i> )	AMPÉROMETRIE POLYIONTU HEPARINU S POUŽITÍM TŘÍFÁZOVÉ ROTUJÍCÍ ELEKTRODY
11:10		Justyna PAWLESA ( <i>I.ročník</i> )	SYNTHESIS OF MWW MATERIALS FOR ADSORPTION PURPOSES
<b>11:30</b>	<b>BREAK</b>		
11:35	<u>Jakub JIRKOVSKÝ</u>	Bhaskaran Nair KIRAN ( <i>I.ročník</i> )	MULTIREFERENCE-BRILLOUIN-WIGNER- COUPLED-CLUSTER CALCULATION OF TITANOCENE SYSTEMS
11:55		Jaroslav CIHELKA ( <i>II.ročník</i> )	APPLICATION OF LASER PHOTOACOUSTIC DETECTION
12:20		Zuzana PAVLAČKOVÁ ( <i>II.ročník</i> )	FORMATION OF MESOPORES IN ZSM-5 BY CARBON TEMPLATING
<b>12:45</b>	<b>Ukončení prvního dne semináře</b>		



**Středa 14.6.2006**

Čas	Předsedající	Přednášející	Název
<b>8:15</b>	<u>Lucie</u> <b>STRÍTESKÁ</b>	Kamil JÍŠA ( <i>II.ročník</i> )	N <sub>2</sub> O DECOMPOSITION OVER Fe/Me- ZEOLITES
8:40		Agnieszka OLŽYŇSKA ( <i>II.ročník</i> )	THE INFLUENCE OF LIPOPOLYTHIOUREAS – RPR209120 AND J5522 – ON THE PROPERTIES OF THE MODEL LIPID MEMBRANE – FLUORESCENCE STUDIES
9:05		Adam MISZTA ( <i>II.ročník</i> )	INTERACTION OF ANTIBACTERIAL PEPTIDES WITH MEMBRANE: A COMBINED ELLIPSOMETRY AND LASER SCANNING MICROSCOPY STUDY
<b>9:30</b>	<b>COFFEE BREAK</b>		
9:45	<u>Kamil</u> <u>JÍŠA</u>	Jakub ŠEBERA ( <i>III.ročník</i> )	DFT CALCULATIONS OF GROUND AND EXCITED STATES OF [Re(L)(CO) <sub>3</sub> (2,2'-bipyridine)] <sup>n+</sup> (L is axial ligand Cl, NCS or pyridine, n=0,1) COMPLEXES, INCLUDING SOLVENT EFFECT
10:10		Jan ŠMYDKE ( <i>III.ročník</i> )	RENNER-TELLER EFFECT INVESTIGATION IN SiCO, CSiO, COSi AND AIOsi
10:35		Tereza KOSTLÁNOVÁ ( <i>III.ročník</i> )	THE EFFECT OF THE INNER PARTICLE STRUCTURE ON THE ELECTRONIC STRUCTURE OF THE NANOCRYSTALLINE Li-Ti-O SPINELS
11:00		Pavel TOPKA ( <i>III.ročník</i> )	DESIGN OF NEW HETEROGENEOUS CATALYSTS FOR ALKENE METATHESIS
<b>11:25</b>	<b>BREAK</b>		
11:30	<u>Pavel</u> <u>TOPKA</u>	Lucie STRÍTESKÁ ( <i>III.ročník</i> )	ACETONITRILE – THE PRESSURE DEPENDENCE OF MOLECULAR PARAMETERS
11:55		Jakub JIRKOVSKÝ ( <i>III.ročník</i> )	PARTICLE SIZE AND SHAPE EFFECT ON THE ELECTROCATALYTIC ACTIVITY OF NANOCRYSTALLINE Ru BASED OXIDE ELECTRODES WITH RUTILE STRUCTURE
12:20		Marie FRYČOVÁ ( <i>III.ročník</i> )	MIX MATRIX MEBRANES BASED ON POLYIMIDS AND MICROPOROUS AND MESOPOROUS SORBENTS
<b>12:45</b>	<b>Ukončení prezentací – přestávka na OBĚD</b>		
<b>15:00</b>	<b>Vyhlášení výsledků a slavnostní ukončení Semináře studentů s přípitkem a malým pohoštěním</b>		





# THE INFLUENCE OF THE PRESENCE OF IONS ON THE WATER ORGANISATION IN THE HEADGROUP REGION OF LIPID BILAYERS: A SOLVENT RELAXATION STUDY

Justyna Barucha

*Martin Hof*

The influence of ions on the organization of biomembranes has been discussed in recent publications based on molecular dynamics simulations [1-3]. In particular the influence of ions with the same charge but different ranking within the Hoffmeister series [4] appears to be of interest. In a series of publications our group showed that the fluorescence solvent relaxation technique provides direct information on amount and mobility of water molecules within phospholipid bilayers [5-7]. Therefore it appears to be a suitable tool for investigating experimentally such possible ion effects.

In this study, unilamellar vesicles composed of dipalmitoylphosphatidylcholine (DOPC) and dipalmitoylphosphatidylserine (DOPS) were labeled with two solvent relaxation probes namely (6-hexadecanoyl-2-(((2-(trimethylammonium)ethyl)-methyl)amino)naphthalene chloride) (Patman) and 4-[(n-dodecylthio)methyl]-7-(N,N-dimethylamino)coumarin (DTMAC) [fig.1], which are known to be located within the phospholipid headgroup region. Using these probes, the influence of two cations ( $\text{Na}^+$  and  $\text{Cs}^+$ ) on the amount of water and its mobility in different z-position within the headgroup region was investigated.

The obtained values for the total amount of the transient Stokes shifts  $\Delta\nu$  show no differences for all investigated systems. The shifts  $\Delta\nu$  are proportional to the polarity of the probed environment. Thus, we conclude that neither the presence of  $\text{Na}^+$  nor of  $\text{Cs}^+$  changes the amount of water present within the headgroup region. On the other hand, the mobility of those water molecules is to some extent influenced by the presence of these cations. While the solvent relaxation kinetics monitored by Patman, which is probing the water molecules bound to the acyl groups is not affected by these ions, the kinetics monitored by DTMAC shows an ion effect: the relaxation kinetic at 20°C for DOPC probed by DTMAC in presence of cesium ions is faster than reference sample with DOPC, DTMAC and water. Studies for sodium ions show kinetic changes which are close to the experimental error. For a molecular interpretation of these experimental results

MD simulations are planned within the framework of a running GAAV grant (Hof/Jungwirth)

- [1] A.A.Gurtovenko, Asymmetry of lipid bilayer induced by monovalent salt: Atomistic molecular – dynamics study. *The Journal of Chemical Physics* 122, 244902 (2005).
- [2] S.A.Pandit, D.Bostick, M.L.Berkowitz, Molecular dynamics simulation of a dipalmitoylphosphatidylcholine bilayer with NaCl. *Biophysical Journal* 84, June 2003, 3743-3750.
- [3] S.A.Pandit, D.Bostick, M.L.Berkowitz, Mixed bilayer containing dipalmitoylphosphatidylcholine and dipalmitoylphosphatidylserine: Lipid complexation, ion binding and electrostatics. *Biophysical Journal* 85, November 2003, 3120-3131.
- [4] F.Hofmeister *Arch. Exp. Pathol. Pharmacol.* 24, (1888) 247-260.
- [5] J.Sýkora, P.Jurkiewicz, R.M.Epand, R. Kraayenhof, M.Langner, M.Hof, Influence of the curvature on the water structure in the headgroup region of phospholipid bilayer studied by the solvent relaxation technique. *Chemistry and Physics of Lipids* 135 (2005) 213-221.
- [6] Hutterer R, Schneider FW, Sprinz H, et al. Binding and relaxation behaviour of Prodan and Patman in phospholipid vesicles: A fluorescence and H-1 NMR study *Biophysical Chemistry* 61 (2-3): 151-160 OCT 30 1996.
- [7] Jurkiewicz P, Sykora J, Olzynska A, et al. Solvent relaxation in phospholipid bilayers: Principles and recent applications, *Journal of Fluorescence* 15 (6): 883-894 November 2005.

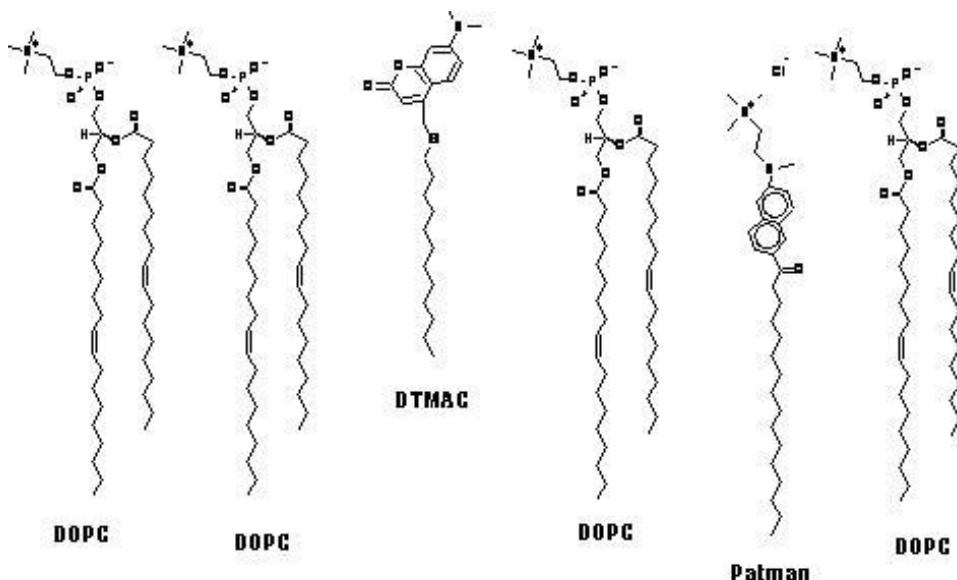


Fig.1  
Distribution of used dyes (Patman, DTMAC), relative to the molecule of dioleoylphosphatidyl choline (DOPC), along the Z-axis of phospholipid bilayer.



## AUTOMATICKÉ GENEROVÁNÍ KÓDU MULTIREFERENCEBNÍ BRILLOUIN – WIGNER METODY VÁZANÝCH KLASTRŮ – TENSOR CONTRACTION ENGINE

**Jiří Brabec**

*Jiří Pittner*

Tensor Contraction Engine (TCE) byl naprogramován S. Hiratou pro automatické generování fortranovského kódu modulu výpočetního balíku NWCHEM a UTCHEM. Symbolicky vyjádřené rovnice ve druhém kvantování překládá do programového kódu. TCE provádí kontrakce kreačních a anihilačních operátorů v souladu s Wickovým teorémem, slučuje stejné členy a redukuje složitost členů násobnými tenzorovými kontrakcemi s permutačními operátory. Narozdíl od staticky napsaného programu lze kód mnohem snáze optimalizovat i vzhledem paralelním výpočtům. V současné době lze pomocí TCE generovat kód pro mnohočástečnou poruchovou metodu (MBPT), metodu konfigurační interakce (CISD, CISDTQ), jednoreferenční metody vázaných klastrů pro různý stupeň excitace (CCD, CCSD, CCSDT, CCSD-TQ) [1-2]. Cílem práce je rozšířit TCE o multireferenční Brillouin-Wigner metodu vázaných klastrů.

### References:

- [1] Hirata, S. and Bartlett, R.J., Chem. Phys. Lett. 321, 216-224, 2000.
- [2] Hirata, S., J. Phys. Chem. A 107, 9887-98, 2003



# APPLICATION OF LASER PHOTOACOUSTIC DETECTION

**Jaroslav Cihelka**

*Svatopluk Civiš*

The development of new GaSb based semiconductor distributed feedback multiple quantum well lasers provides a tunable source of radiation with high spectral purity in temperature range 0 – 60 °C. These new types of lasers comply with the requirements for sources of radiation in high-resolution molecular spectroscopy: continuous wave emission, high power (more than 1 mW), low optical noise and high wavelength tunability ( $20 \text{ cm}^{-1}$ ). The rapid tunability of these lasers is an important property that can be used in the study of chemical reactions, monitoring of fast processes or detection of molecular ions or short-lived radicals.

The development of technology has permitted the preparation of tunable lasers working in the C-H and N-H overtones regions (2,3  $\mu\text{m}$ ).

This work is concerned with the testing of GaSb lasers, which have been proposed for application in an atmospheric gas detection.

An investigation of photoacoustic detection using 2,3  $\mu\text{m}$  diode lasers is described. An inexpensive resonant photoacoustic system was developed based, on a simple glass cell with resonator tube and microphone (Knowles EK-3024). The system was tested on the single rotation-vibration lines of  $\text{CH}_4$ ,  $\text{N}_2\text{O}$  and  $\text{NH}_3$  gases. The best detection limits obtained are 0,1 ppm for  $\text{NH}_3$  and 50 ppm for  $\text{CH}_4$ . Potential applications of infrared diode laser photoacoustic detection lies in the areas of analytical chemistry, atmospheric research, and investigation of the kinetics of reactive species.





# PALLADIUM NANOPARTICLES GRAFTED ONTO MESOPOROUS MOLECULAR SIEVE MCM-41

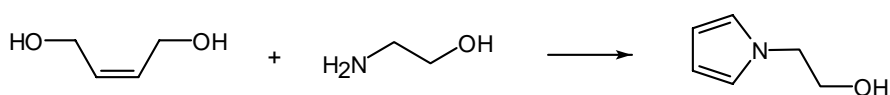
Jan Demel

*Jiří Čejka*

In last decades metal nanoparticles have been extensively studied due to their unique properties such as high surface-to-volume ratio. Several methods for preparation of palladium nanoparticles have been developed. The most convenient route is represented by reduction of various palladium(II) compounds in the presence of stabilizing agents such as poly(vinylpyrrolidone), tetraalkylammonium salts or polar solvents like propylene carbonate that prevent aggregation of the metal particles [1].

The first mesoporous molecular sieves with very narrow pore size distribution were synthesized at Mobil Research and Development Corporation in early 1990's. This novel family of materials was obtained by using micelles as structure-directing agents [2]. These materials have attracted attention as solid supports for reusable catalysts.

In our work we have prepared palladium nanoparticles by reduction of palladium(II) acetate in the presence of two different stabilizing agents: propylene carbonate and tetrabutylammonium acetate. Those palladium nanoparticles were grafted onto mesoporous molecular sieve MCM-41. The novel catalysts obtained were tested in reaction of cis-butene-1,4-diol and 2-aminoethanol to give N-(2-hydroxyethyl)pyrrol.



This elegant one-step method for preparation of N-substituted pyrrols was originally reported to be catalyzed by palladium metal [3]. Both our catalysts showed good catalytic activity under relatively mild conditions.

This work was financially supported by the Grant Agency of the Czech Republic grant nos. 104/05/0192, 203/03/H140, and LC06070.

## References

- [1] Reets M., de Vries J., Chem. Comm. **2004**, 1559
- [2] Kresge C. T., Leonowicz M. E., Roth W. J., Beck J. S., Nature **1992**, 359, 710
- [3] Muharashi S., Shimamura T., Moritani I., Chem. Comm. **1974**, 931



## **MIX MATRIX MEBRANES BASED ON POLYIMIDES AND MICROPOROUS AND MESOPOROUS SORBENTS**

**Marie Fryčová**

*Milan Kočířík*

Mixed matrix materials comprising molecular sieve entities embedded in a polymer matrix can economically increase membrane permselectivity, thereby addressing a key challenge hindering the widespread use of membrane-based gas separations. It has already been demonstrated that the incorporation of microporous inclusions such as zeolites into a polymer matrix results in an improvement of the gas separation properties of the material used in the form of a membrane. However, when a polymer in the glassy state at room temperature is used, adhesion between the polymer phase and the external surface of the particles appeared to be a major problem in the preparation of such membranes. The quality of interfacial contact zone appears to be equally important to achieve sufficient membrane cohesiveness and integrity on one side and appropriate transport properties on the other.

The aim of my PhD work is preparation of various useful mixed matrix membranes and examine membrane material properties such as cohesiveness, integrity and their permeability for small gas molecules.

It was suggested that a promising way to prepare PI-zeolite composites with an adequate interfacial adhesion would be that one based on the application of a coupling agent. Thus, 3-Aminopropyltriethoxysilane (APTES) was used as the coupling agent. In the first step an APTES terminated polyimide precursor was prepared. Its coupling ability is related to condensation reactions of ethoxy groups on terminated polymer with OH groups at zeolite outer surface. The advantage of the selected approach is that a penetration of coupling agent into the pores of sorbents is reduced due to size exclusion effect.

New mixed matrix materials based on various polyamides and sorbents were prepared based on previous experience. The non-stationary permeation tests are carried out with helium and/or nitrogen by using a semi-open permeation apparatus.

# DNA CONDENSATION INFLUENCED BY COUNTERIONS – FLUORESCENT CORRELATION SPECTROSCOPY APPLICATIONS

**Barbara Gasińska**

*Martin Hof*

Major and minor grooves of the B-DNA exhibit ionophore-like properties and arrange cations in a specific way along plasmid strain. Such ions are important for DNA stability and can also serve as sensitive electrostatic probes to map the dynamic surface of DNA for macromolecular recognition. The location of direct binding sites depends mostly on the character of the ions and their concentration.

We show that Fluorescence Correlation Spectroscopy (FCS) is a suitable tool for the detection of the DNA binding of positively charged ions from Hofmeister series. In particular we are investigating DNA condensation induced by those ions. Condensation of the bacterial plasmid B-DNA (10kpb) was observed already for very low ( $C_{\text{salt}}/C_{\text{DNA phosphate}}=10^3$ ) concentration of the  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Cs}^+$  ions. For this purpose DNA molecules were labeled with Pico Green (an ultra-sensitive fluorescent nucleic acid stain).

The FCS technique by collecting a large number of single molecule measurements gives possibility to differentiating measuring particles as regards hydrodynamic size. In FCS contrary to the other fluorescence techniques the most interesting parameter is not fluorescence emission intensity, but spontaneous intensity fluctuations which are then described by the autocorrelation function. By the fitting procedure the autocorrelation function provides such parameters as: diffusion time, count rate and particle number. With decreasing hydrodynamic size of the DNA molecule the diffusion constant increases, which is the main indicator of plasmid condensation.

# **ODHAD DISTRIBUCE TĚŽKÉHO ATMOSFÉRICKÉHO POLUTANTU V MĚSTSKÉ AGLOMERACI S VYUŽITÍM CO<sub>2</sub> – LASEROVÉ OPTOAKUSTICKÉ METODY V NÍZKORYCHLOSTNÍM AERODYNAMICKÉM TUNELU**

**Eva Grigorová**

*Zdeněk Zelinger*

Metodou Fourier-transform infračervené spektrometrie byla změřena absorpční spektra vybraných modelových atmosférických škodlivin - plynného fluoridu sírového a plynného ethanolu. Ve změřených spektrech byly identifikovány základní vibrační módy molekul těchto látek. Pomocí laser-diodové infračervené spektrometrie bylo sledováno tlakové rozšíření absorpčních pásů daných látek a v obdržených spektrech demonstrována interference s emisními liniemi <sup>12</sup>CO<sub>2</sub>-laseru v 9-10 μm-ové oblasti. Dále bylo testováno využití metody CO<sub>2</sub>-laserové optoakustické detekce (LOAD) při fyzikálním modelování disperze těžkého plynu na modelu městského měřítká umístěném v nízkorychlostním aerodynamickém tunelu (proměření kalibračních křivek, stanovení absorpčního koeficientu SF<sub>6</sub>, stanovení meze detekce aparatury, monitorování koncentrace polutantu ve vybraných bodech modelu při několika referenčních rychlostech proudění v tunelu). Obdržené výsledky byly porovnány s údaji o distribuci plynného ethanolu, získanými pomocí metody LOAD, a s údaji o distribuci ethanu, jehož koncentrace byly stanoveny plamenově ionizačním detektorem.



## **PARTICLE SIZE AND SHAPE EFFECT ON THE ELECTROCATALYTIC ACTIVITY OF NANOCRYSTALLINE Ru BASED OXIDE ELECTRODES WITH RUTILE STRUCTURE**

**Jakub Jirkovský**

*Petr Krtil*

The electrochemical behavior of ruthenium dioxide based materials has been investigated with respect to chlorine evolution reaction (CER), oxygen evolution reaction (OER) and hydrogen evolution reaction (HER). Electrocatalytic behavior of  $\text{RuO}_2$  was studied on both single crystal as well as polycrystalline electrodes. Unfortunately, the experiments carried on the single crystals so far reflect the behavior of just two orientations and provide no information about the contributions from crystal edges. The data published about electrocatalytic behavior of polycrystalline  $\text{RuO}_2$  on the other hand, cannot be related to actual orientation and quality of the surface. Despite the great effort devoted to characterization of the polycrystalline and single crystal electrodes so far, the nature of the active sites for either reaction (i.e. their corresponding local or crystallographic environments) remains unknown. This paper focuses on the connection between the nanocrystalline particle size/shape and the electrocatalytic activity of two oxide systems;  $\text{RuO}_2$  and  $\text{Ru}_{0.8}\text{Co}_{0.2}\text{O}_{2-x}$  solid solution.

The  $\text{RuO}_2$  and  $\text{Ru}_{0.8}\text{Co}_{0.2}\text{O}_{2-x}$  powders were prepared by a sol-gel synthesis forming amorphous precursor followed by annealing at temperatures 400-900 °C. Samples were analyzed using X-ray diffraction (XRD) and high resolution transmission electron microscopy (HRTEM). All samples were of single phase character with mean particle size ranging between 15 and 60 nm. The shape of the prepared nanocrystals extracted from the HRTEM data varies for the prepared materials between rod-like and isometric one. Regardless of the actual shape the crystals feature prismatic part (composed of  $\{110\}$  and  $\{100\}$  oriented faces) and pyramidal parts (composed of  $\{101\}$  oriented faces). The electrochemical activity was examined by means of differential electrochemical mass spectrometry (DEMS).  $\text{RuO}_2$  and  $\text{Ru}_{0.8}\text{Co}_{0.2}\text{O}_{2-x}$  based electrodes show different activity in OER and parallel OER and CER reactions. If only OER may proceed at the electrode one observes a decrease of  $\text{O}_2$  production with increasing particle size of  $\text{RuO}_2$ . The same reaction on  $\text{Ru}_{0.8}\text{Co}_{0.2}\text{O}_{2-x}$  shows opposite size related trend. This indicates different role of crystal edges in electrocatalytic activity of both systems. In the case of parallel OER and CER both electrode materials show increased selectivity toward  $\text{Cl}_2$  evolution with increasing particle size. In the case of  $\text{RuO}_2$  this behavior results from simultaneous OER suppression. In the case of  $\text{Ru}_{0.8}\text{Co}_{0.2}\text{O}_{2-x}$  is the selectivity improvement less dramatic and corresponds to higher activity of bigger nanocrystals to CER.



## **N<sub>2</sub>O DECOMPOSITION OVER Fe/Me- ZEOLITES**

**Kamil Jiša**

*Zdeněk Sobalík*

Nitrous oxide (N<sub>2</sub>O) is potent greenhouse gas that contributes to ozone layer depletion. N<sub>2</sub>O from nitric acid production is one of the largest sources of N<sub>2</sub>O in chemical industry and nowadays there is a quest to find and develop efficient and economical system for N<sub>2</sub>O abatement. One way is direct catalytic decomposition of N<sub>2</sub>O to N<sub>2</sub> and O<sub>2</sub> over metal-exchanged zeolites. Fe-zeolites are among perspective catalysts for N<sub>2</sub>O decomposition but suffer from strong deactivation under realistic conditions due to presence of H<sub>2</sub>O in the tail gas from nitric acid production. It has been found that higher catalyst activity in N<sub>2</sub>O decomposition could be achieved by combining Fe-zeolites with noble metals.

NH<sub>4</sub>-ferrierite (Si/Al 8.5 TOSOH Co.) was used as a parent zeolite. Fe-FER catalysts were prepared by an impregnation of NH<sub>4</sub>-FER with FeCl<sub>3</sub> in acetyl-acetone. Noble metal ions in Pt-, Rh- and Ru-FER catalysts were introduced into NH<sub>4</sub>-FER by ion-exchange with solution of Pt, Rh and Ru complexes in water. Bimetallic catalysts (Fe/Pt-, Fe/Rh-, Fe/Ru-FER) were prepared by ion-exchange of noble metal and then Fe ions were introduced, respectively. The catalytic activity was studied with 100 mg of the sample in a quartz U-shaped micro reactor. The composition of reaction mixture was 1000 ppm N<sub>2</sub>O, 25 – 1000 ppm NO, 3 vol.% O<sub>2</sub> and the rest He. Concentration of N<sub>2</sub>O and NO<sub>x</sub> in the outlet of the reactor was analysed by IR analyser (Advance optima ABB Co.) and chemiluminescent analyser (MLU 200AH).

It has been proven that Fe-zeolites are not sufficient catalyst for N<sub>2</sub>O decomposition under realistic conditions. Further addition of Fe ions into NH<sub>4</sub>-ferrierite has only small positive effect on N<sub>2</sub>O decomposition. Addition of O<sub>2</sub> into reaction mixture causes a slight decrease in conversion. The addition of noble metals into Fe-ferrierite catalyst increased its activity in N<sub>2</sub>O decomposition, both in absence or presence of NO in the reaction mixture and the synergistic effect between noble metals and iron was observed. Fe/Rh-FER was the most active catalyst.

Stable oscillation behaviour of N<sub>2</sub>O decomposition was evidenced for all bimetallic catalysts that disappeared after NO addition into reaction mixture. Similar oscillatory changes were observed over Fe-FER but after a rather long period than over Fe/Me-FER.



# MULTIREFERENCE-BRILLOUIN-WIGNER- COUPLED-CLUSTER CALCULATION OF TITANOCENE SYSTEMS

**Kiran Bhaskaran Nair**

*Jiří Pittner*

Titanocene systems are interesting for homogeneous catalysis. Many of these systems have degenerate orbitals and show a multireference character.

Multireference Brillouin-Wigner Coupled Cluster (MR BWCC) approach [1] is an ab initio method for accurate treatment of systems, in which the electronic state is degenerate or quasi-degenerate. This method has been successfully implemented into the ACES II program package and has been shown to be able to describe satisfactorily many chemical systems.

Multireference Brillouin-Wigner Coupled Cluster (MR BWCC) approach is used to study the staggered and eclipsed conformers of both methyl substituted and non-substituted titanocene. From CASSCF studies it is clear that the singlet state of both these conformers has a multireference character. Our aim is to determine the accurate electronic structure of titanocene systems and to study the singlet-triplet splitting.

References:

- [1] Petr Čársky, Jiří Pittner, Ivan Hubač  
Multireference Coupled Cluster Method Based on the Brillouin-Wigner Perturbation Theory  
C. F. Dykstra, G. Frenking, K. S. Kim, and G. B. Scuseria (eds.), pp. 465--481,  
Elsevier, Amsterdam, The Netherlands (2005).



## THE EFFECT OF THE INNER PARTICLE STRUCTURE ON THE ELECTRONIC STRUCTURE OF THE NANOCRYSTALLINE Li-Ti-O SPINELS

Tereza Kostlánová

*Petr Krtil*

Nano-crystalline oxides belong to prospective electrode materials for the rechargeable batteries. The high specific surface area of these nanocrystalline materials allows to construct electrodes delivering the desired current output at decreased actual current density. In addition to that the decrease of the characteristic particle size leads to a decrease of characteristic diffusion lengths, which shortens the time necessary for complete charge/discharge of the electrode. The utilization of these advantages is based on assumption that the insertion into nano-crystalline hosts follows the same mechanism as that into micro-crystalline hosts. This assumption, however, must not be always true.

The effect of the inner particle structure on Li insertion activity and electronic structure of the nanocrystalline Li-Ti-O spinels was studied on materials prepared by solid state and solvothermal synthesis. The high temperature prepared materials of composition  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  feature particle size of ca. 200nm. The products of solvothermal synthesis with composition  $\text{Li}_{1.1}\text{Ti}_{1.9}\text{O}_{4+\delta}$  feature cubic particles of characteristic dimension of ca. 50 nm. The characteristic particle size differs from that of the coherent domain size determined by X-ray diffraction.

The reduction of the solvothermal and high temperature synthesized spinels in Li containing solutions leads according to  $^6\text{Li}$  MAS NMR spectra to Li insertion into tetrahedral 8b and octahedral 16c position, respectively. Additional broad NMR signal attributable to a Knight shift was observed in spectra of partially reduced high temperature spinels. In the case of solvothermal spinels is the Knight shift signal less pronounced and appears only in spectra of samples in which the phase transition occurs on the local level. The UV-Vis-NIR spectra of the partially reduced Li-Ti-O spinels correspond to expected semiconductor character of Li-Ti-O oxides. Both materials are characterized by wide band gap of 3.8 eV (high temperature spinel) and 3.5 eV (solvothermal material). Partial reduction accompanied with Li insertion causes additional optical transition in the visible to near infrared region, which can be attributed to formation of trivalent Ti. The behavior observed for partially reduced high temperature spinels is similar to that reported for  $\text{TiO}_2$  (anatase)<sup>1</sup>. The spectral behavior of the partially reduced solvothermal spinels is more complex and reflects higher localization of the inserted electrons due to suppressed phase transition.

1. J.K. Burdett, T. Hughbanks, *Inorg. Chem.* 24 (1985),1741.





## **INTERACTION OF ANTIBACTERIAL PEPTIDES WITH MEMBRANE: A COMBINED ELLIPSOMETRY AND LASER SCANNING MICROSCOPY STUDY**

**Adam Miszta**

*Martin Hof*

Magainin 2 and Melittin belong to the family of antibacterial peptides. These  $\alpha$ -helical peptides are considered to kill bacteria by permeabilizing and/or disrupting bacteria's membrane. They are rather well studied peptides with positive charged aminoacids. They interact preferentially with acidic lipids, which are particularly abundant in bacteria's membrane. The "toroidal model" describes the interaction of Magainin 2 and Melittin with the membrane. This model assumes that the antimicrobial peptides are able to create the pores and then destroy the membrane.

In my study I used two different optical techniques (Ellipsometry and Laser Scanning Microscopy) to investigate the interaction of antibacterial peptides with supported phospholipids bilayers.

The ellipsometry was used to characterize the kinetics of the interaction between peptides and membranes. From this technique the surface mass, thickness and refractive index of surface were obtained. The laser scanning microscopy was used to obtain high resolution images of the supported membrane with peptides.

The results obtained from ellipsometry showed that antibacterial peptides destroy the supported phospholipids bilayers. This effect for each peptide is different. Magainin 2 during the penetrating removes the lipids from the membrane very fast what we observe as decreasing of surface mass. Whereas Melittin after penetrating creates with the lipids the aggregates what we observe as increasing of surface mass.

To better understand the ellipsometry results the interaction of these peptides with membrane were monitored by Laser Scanning Microscopy using labelled with Oregon Green SPBs.

# VLIV NOSIČE NA SEPARAČNÍ VLASTNOSTI MEMBRÁN

Vladimír Navara

*Arlette Zikánová*

Práce se zabývá studiem porézních těles z hlediska jejich použitelnosti jako nosičů zeolitických membrán. Práce si klade za cíl přispět k vývoji efektivní metodiky jejich charakterizace, které by bylo možno následně využít k vyhodnocení vlivu keramických nosičů na separační vlastnosti kompozitních zeolitických membrán. V této úvodní části studia se výzkum zaměřuje na nosiče planárních membrán na bázi  $\text{Al}_2\text{O}_3$  a je sledována souvislost transportně strukturních parametrů nosičů s technologickými parametry jejich přípravy. K charakterizaci je využito rtuťové porozimetrie, měření „bubble pointu“, skenovací elektronové mikroskopie (SEM) a jedno- a dvousložkových permeačních měření.

Na základě získaných dat byl určen vliv dvou parametrů výroby nosičů tj. doby mletí vstupních surovin a teploty výpalu na kvalitu nosičů membrán.

Na studovaných nosičích byly syntetizovány zeolitické vrstvy a na základě vícesložkových permeačních měření byl zjištěn vliv nosiče na transportní charakteristiky kompozitních membrán.

# THE EFFECT OF SUPPORT ON THE SEPARATION PROPERTIES OF MEMBRANE

**Vladimír Navara**

*Arlette Zikánová*

This work deals with the study of porous bodies in relation to their applicability as supports of zeolitic membranes. The aim of the study was to contribute to the development of effective characterization methods suitable for evaluation of the effect of ceramic supports on separation properties of composite zeolitic membranes. In this initial study the focus was on planar membrane supports based on  $\text{Al}_2\text{O}_3$ . The principal goal of the study was to establish a relation between transport-related structural parameters and technological parameters of support preparation. The characterization methods used were mercury porosimetry, bubble point measurement, scanning electron microscopy (SEM) and one- and two- component permeation measurements.

The effect of two support preparation parameters i.e. that of raw material grinding time and sintering temperature was estimated on the basis of experimental results.

The zeolitic layers were synthesized on the studied supports. The influence of support on transport characteristics was investigated by means of multi component permeation experiments.



# MICROWAVE AND HYDROTHERMAL SYNTHESIS OF MCM-41 AND MCM-48 WITH TIN FOR BAEYER-VILLIGER REACTION

Iveta Nekoksová

*Jiří Čejka*

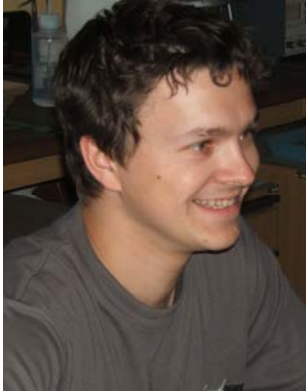
Baeyer-Villiger reaction is oxidation of ketones to respective esters and cyclic ketones to lactones. The reaction possesses a lot of applications and the synthesis importance is considerable, e.g. in pharmacy, perfumery. Corma et al. showed [1] that heterogeneous catalysts like zeolites and mesoporous molecular sieves with tin as a Lewis acid centre seem to be a promising catalyst for this reaction. The benefit of this system is especially selective activation of carbonyl group and using hydrogen peroxide as oxidation agent.

The aim of this work was to synthesize MCM-41 and MCM-48 with different content of tin in structure by hydrothermal and microwave approaches, to characterize these materials (by XRD, N<sub>2</sub> adsorption, pyridine adsorption measured by FTIR) and to test them in Baeyer-Villiger oxidation of selected cyclic ketones (adamantanone, norcamphor, cyclohexanone, cyclohex-2-en-1-one).

The reaction with hydrogen peroxide was investigated in a liquid phase at the reaction temperature of 50 °C. The conversion of adamantanone was around 75-100 %, the conversion of norcamphor around 50-85%, of cyclohexanone around 45-60 % and of cyclohex-2-en-1-one around 35-45 %, all with selectivity to the lactone product near 100 %, depending on the type of preparation of the catalyst, incorporation of tin and a partial collapse of the structure of mesoporous molecular sieve with increasing amount of tin. Generally, catalysts prepared by microwave synthesis possessed a higher catalytic activity, better incorporation of tin and higher hydrothermal stability compared with the same catalyst prepared by hydrothermal synthesis.

## References:

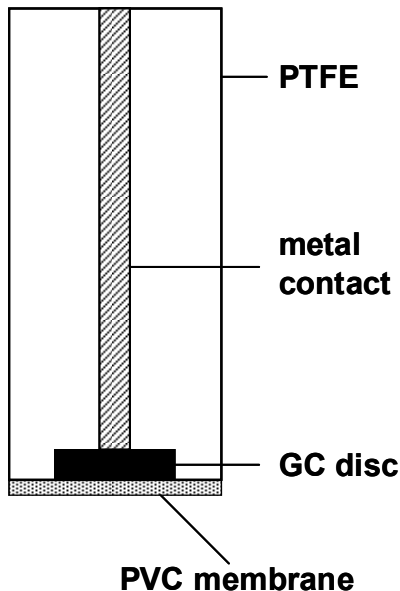
- [1] Corma A., Nemeth L.T., Renz M., Valencia S., Nature, 412 (2001) 423.



# AMPÉROMETRIE POLYIONTU HEPARINU S POUŽITÍM TŘÍFÁZOVÉ ROTUJÍCÍ ELEKTRODY

Jiří Olšák

Zdeněk Samec



Elektroda složená ze skelného uhlíku (GC) pokrytého PVC membránou plastifikovanou o-nitrofenyloktyléterem (o-NPOE) nebo bis(2-etylhexyl) sebakátem (DOS) byla použita pro ampérometrickou resp. coulometrickou detekci heparinu přítomného ve vodném roztoku 0,1 M LiCl resp. krevní plazmě v koncentracích používaných v lékařské praxi k dosažení antikoagulačního účinku (1-10 U/ml). Membrána obsahovala 1,1'-dimetylferocén (DMFc 0,01 M, přenašeč elektronu) a hexadecyltrimetylamonium tetrakis (4-chlorfenyl) borát (HTMATPBCl 0,05 M, nosný elektrolyt) nebo tridodecylmetylamonium tetrakis (4-chlorfenyl) borát (TDMATPBCl 0,05 M) a byla nanášena na povrch skelného uhlíku technikou "spin coating". Tímto způsobem bylo možno reprodukovatelně připravovat membránu o definované tloušťce (20-100  $\mu\text{m}$ ).

Analýza voltametrických dat nás vede k závěru, že klíčovým krokem detekčního mechanismu je potenciálová závislost reversibilní adsorpce iontového páru, vytvářeného mezi polyaniontem heparinem a kationtem ( $\text{HTMA}^+$ , resp.  $\text{TDMA}^+$ ) na rozhraní membrána | roztok elektrolytu, která je spřažena s oxidací DMFc na povrchu GC elektrody.



# THE INFLUENCE OF LIPOPOLYTHIOUREAS – RPR209120 AND J5522 – ON THE PROPERTIES OF THE MODEL LIPID MEMBRANE – FLUORESCENCE STUDIES

Agnieszka Olżyńska

*Martin Hof*

In many recent studies, lipoplexes (natural or synthetic nucleic acids complexed with lipids) have proved their usefulness for the gene therapy and the number of positively charged lipids used in lipofection (liposome-mediated transfection) still increases. These synthetic gene transfer tools seem to be safer than the viral one, however, they are not devoid of several disadvantages. Because of the positive charge present on a cationic lipid, lipoplexes can interact with negatively charged extracellular components of cells, for example. Therefore, neutral compounds that would create complexes with nucleic acids seem to be of a great importance. Beside many commercially available transfection reagents, many of newly synthesized ones are constantly investigated with a great attention.

We believe that composition and structure of liposome bilayer can influence formation of lipoplexes and efficiency of transfection.

In this work, the large unilamellar vesicles (LUVs) composed of DOPC (dioleoylphosphatidylcholine) and RPR209120 (cationic compound) or J5522 (neutral compound) (rys. 1), were studied. These two synthesized lipids are currently evaluated for their *in vitro* and *in vivo* transfection activity by Nathalie Mignet and co-workers.

To determine the properties of the lipid bilayer in the headgroup region, the solvent relaxation (SR) technique was employed. Solvent relaxation refers to dynamic reorganization of solvent molecules as a response to a rapid change in the fluorescent dye electric charge distribution during excitation process. The overall Stokes shift gives the information on the polarity of the vicinity of the probe (naphthalene derivatives 6-hexadecanoyl-2-(((2-(trimethylammonium)ethyl)methyl)amino)naphthalene chloride (Patman) and 6-dodecanoyl-2-dimethylaminonaphthalene (Laurdan) were used in this study) in the bilayer. Moreover, the kinetics of the Stokes shift reflects mobility of the dye environment.

The results show that J5522 and RPR209120 influence the lipid bilayer properties in different manner. It seems that J5522 causes DOPC bilayer to be less fluid, while lipid membrane with RPR209120 does not show such behaviour.

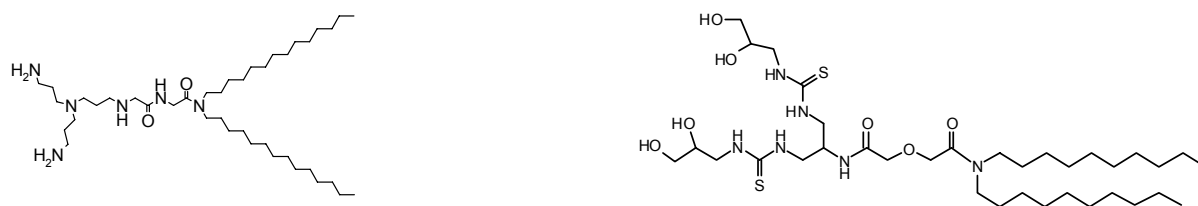


Fig. 1. RPR209120 (left); J5522 (right)



## FORMATION OF MESOPORES IN ZSM-5 BY CARBON TEMPLATING

Zuzana Pavlačková

*Jiří Čejka*

Zeolite ZSM-5 is the most frequently applied zeolite catalyst in the chemical technology [1,2]. Sometimes the presence of micropores can also limit catalytic performance of zeolites, especially when the diffusion is the rate-determining step of the overall chemical reaction [3]. A new route how to prepare mesoporous single crystal is based on the utilization of small carbon particles with narrow particle size distribution, which are added to the synthesis mixture for the preparation of zeolite [4]. After the synthesis, carbon black is removed from each individual crystal by combustion, which leads to the formation of well-defined zeolite single crystals with mesopores of the size which correspond to the size of carbon black.

The main goal of this study is to find the way how to control the amount of formed mesopores in ZSM-5 by addition of carbon black. The porous structure of such prepared zeolites was characterized by different experimental techniques (X-ray powder diffraction, scanning electron microscopy, nitrogen physisorption and FT-IR spectroscopy).

The results showed that the carbon particles act as a secondary structure-directing agent for creating mesopores. The X-ray diffractograms confirmed that all samples contain exclusively ZSM-5 zeolite phase. From the scanning electron micrographs it is clearly seen that ZSM-5 particles are of uniform size and relatively well shaped. An interesting roughness on the outer surface of each individual single crystal was observed. The adsorption measurements evidenced that the generation of mesopores depends on the amount of carbon which was added to the synthesis. The higher is the amount of carbon, the higher is mesopore volume and the mesopore diameter is comparable to carbon particle diameter which was used.

### References

- [1] J.N. Armor, Appl. Catal. A 222 (2001) 407.
- [2] W.J. Roth, J.C. Vartuli, in J.Čejka, H. van Bekkum (Eds), Zeolites and Ordered Mesoporous Materials: Progress and Prospects, Stud. Surf. Sci. Catal. 157 (2005) 91.
- [3] J. Čejka, B. Wichterlová, Catal. Rev. 44 (2002) 375.
- [4] C.J.H. Jacobsen, C. Madsen, J. Houzvicka, I. Schmidt, A. Carlsson, J. Am. Chem. Soc. 122 (2000) 7116.



## SYNTHESIS OF MWW MATERIALS FOR ADSORPTION PURPOSES

Justyna Pawlesa

*Jiří Čejka*

Micro- and mesoporous molecular sieves have attracted in recent decades substantial interest as adsorbents and catalysts resulting in a high number of industrial processes. In this contribution we report on the isotherm adsorption measurements carried out with different alkali-metal forms of microporous MCM-22 materials.

The synthesis and characterization of MCM-22 and MCM-49 zeolites have been done. MCM-22 was synthesized in the range of initial Si/Al molar ratios from 15 to 40, with hexamethylenimine as organic template. In order to study on the parameters controlling the formation of the MCM-49, the samples with different Si/Al ratios and different molar ratios (Ro/Ri) of the organic template (Ro) to the inorganic cations (Ri) have been prepared.

The syntheses were carried out under agitation at 150 °C for 5 days. The samples were calcined at 550 °C for 6 hours. Various alkali ion forms ( $M = \text{Na}^+, \text{K}^+, \text{Li}^+, \text{Cs}^+$ ) of MCM-22 with different Si/Al ratios were obtained by treatment with 0.5 M  $\text{MNO}_3$  (and LiCl in case of  $\text{Li}^+$  form) for adsorption measurements.

The prepared materials were characterized by X-ray powder diffraction, scanning electron microscopy (SEM) and chemical analysis. The samples were modified by means of ion-exchange ( $\text{NH}_4^+$ ) and characterization of type and concentration of active sites have been determined by FTIR of adsorbed  $\text{d}_3$ -acetonitrile.

Nitrogen and carbon dioxide adsorption isotherms of the porous samples were measured with a Micrometrics ASAP 2020 volumetric instrument at 77 K and 273 K, respectively.





## ACETONITRILE – THE PRESSURE DEPENDENCE OF MOLECULAR PARAMETERS

Lucie Střiteská

Štěpán Urban

Acetonitrile is a well known frequently studied molecule that was chosen to perform testing measurements of our new “Prague mm-wave Spectrometer”. Acetonitrile rotational transitions were measured in the whole spectral range of our spectrometer from  $J'' \leftarrow J' = 1 \leftarrow 0$  (18 GHz) to  $J'' \leftarrow J' = 15 \leftarrow 14$  (275 GHz). The sample pressure range was 0.5 to 50  $\mu$ bar, each spectral line was measured at 3 different values of pressure at least. There were observed resolved or partly resolved hyperfine structures of rotational transitions.

The data measured were treated first to obtain the hyperfine pressure parameters  $eQq_0$ ,  $eQq_J$ ,  $C_N$ ,  $C_N - C_K$  and the “hyperfine-free” rotational transition frequency parameters  $\nu(J,k)$ . Then the “hyperfine-free” rotational transition frequencies were treated to obtain the rotational constant  $B$  and the centrifugal distortion constants  $D_J$ ,  $D_{JK}$ ,  $H_{JJ}$ ,  $H_{JK}$ ,  $H_{KJ}$  and  $L_{JJJ}$ . The data measured at different pressures were treated by this manner separately.

As a result, the linear pressure dependencies of all the molecular parameters were obtained. These molecular constants have a very close relationship to molecular geometry. This means, that we can discuss the pressure effect on the molecular geometry of acetonitrile. Unfortunately, we miss information on values of some constants because of the symmetric top selection rules and therefore the molecular geometry changes cannot be fully quantified. Also the centrifugal distortion effects on the molecular geometry can be discussed correctly only in the case  $K=0$ . More detailed discussion can be found in (1).

(1) Pressure Shifts of Acetonitrile Ground State Parameters: P. Kania, L. Střiteská, M. Šimečková, and Š. Urban, *J. Mol. Structure*, accepted.



# DFT CALCULATIONS OF GROUND AND EXCITED STATES OF $[\text{Re}(\text{L})(\text{CO})_3(2,2'\text{-bipyridine})]^{n+}$ (L is axial ligand Cl, NCS or pyridine, n=0,1) COMPLEXES, INCLUDING SOLVENT EFFECT.

Jakub Šebera

*Stanislav Zális*

The flexibility of the coordination sphere of mixed valence carbonyl complexes enables us to tune spectral and photochemical properties. The lowest lying excitations within mixed-ligand metal carbonyls  $[\text{Re}(\text{L})(\text{CO})_3(\text{bpy})]^{n+}$ , connected with a large electron density redistribution, have been traditionally described as metal to ligand (MLCT) or ligand to ligand (LLCT) charge transfer transitions. In order to explain correctly spectroscopy and excited states (ES) behaviour of carbonyl-diimine complexes there is necessary to describe these states and their mixing properly. The character of axial ligand L influences substantially MLCT – LLCT mixing, therefore, the electronic structure of series of complexes involving different ligands L was studied in order to explain the variation of spectral properties.

In order to characterize how the particular lowest excited state reflects the coordination sphere variation, a combined experimental and theoretical study was performed. The interpretation and modelling of experimentally measured UV-vis emission, picosecond time-resolved IR spectra are based on DFT calculations.

The ground state electronic structures were calculated by using the density functional theory (DFT) method. The spectral transitions and charge density redistributions in the course of excitations were calculated by the time-dependent DFT (TD-DFT) method. The lowest excited states of the closed-shell complexes were optimized at TD-DFT level or unrestricted Kohn-Sham calculations on the lowest-lying triplet state. The electrostatic solvent influence on spectra was modelled using the polarizable – continuum model (PCM) or conductor – like screening model (COSMO). The interpretation of ground and excited state IR spectra was based on the vibration analysis at optimized structures. The quantum chemistry calculations were performed using Gaussian and Turbomole program packages.

The DFT calculated structures, ground and excited state IR spectra, and UV-vis spectra correspond qualitatively well to the experimental data.



## RENNER-TELLER EFFECT INVESTIGATION IN SiCO, CSiO, COSi AND AIOsi

Jan Šmydke

*Jiří Pittner*

Linear triatomic molecules SiCO, CSiO, COSi (singlet, triplet) and AIOsi (doublet, quartet) have been calculated to investigate the singlet-triplet (doublet-quartet) gaps and the Renner-Teller splitting.

The wavefunction of linear molecules with nonzero angular momentum component about the molecular axis ( $\Pi$ ,  $\Delta$ , ... terms) is degenerate. The degeneracy however splits when the molecule is bent from its linear shape. This splitting is known as the Renner-Teller effect.

Harmonic vibrational frequencies of triatomic linear molecules involve two degenerate perpendicular bending modes. It can be shown that in the Renner-Teller case each of their calculated values corresponds to the different split wavefunction. As a result we can obtain four different vibrational frequencies of the molecule.

The equilibrium geometries and the harmonic vibrational frequencies were obtained by the CASSCF method in the cc-pVTZ basis set. The singlet-triplet (doublet-quartet) gaps were calculated by CCSD and 2R BW CCSD methods in the same basis.



## DESIGN OF NEW HETEROGENEOUS CATALYSTS FOR ALKENE METATHESIS

**Pavel Topka**

*Jiří Čejka*

Alkene metathesis is a reaction, which has found many applications in modern chemical synthesis. In the presence of certain transition-metal compounds (mainly Re, Mo, Ru and W), alkylidene fragments around the C=C double bond are redistributed, which enables transformation of low value feedstocks into useful chemical products such as important polymers, oleochemicals, specialty chemicals and petrochemicals. Tungsten, molybdenum and rhenium oxides supported on silica or alumina are used as metathesis catalysts. Heterogeneous catalysts remain the preferred choice for industrial applications because of their easier regeneration and separation from the reaction mixture.

We developed new types of heterogeneous metathesis catalysts which were prepared by supporting molybdenum oxide on mesoporous silicas. In metathesis of 1-octene as a model substrate, our catalysts showed considerably higher activity compared with catalysts supported on conventional silica. With the most active catalyst, MoO<sub>3</sub>/MCM-41 with 6 wt. % of Mo, 75 % conversion of 1-octene and 84 % selectivity to 7-tetradecene was achieved after 360 min of the reaction at 40 °C. No solvent was required for the reaction, which made the separation of the products much easier. Using Raman spectroscopy it was shown that catalytic activity correlates with the amount of isolated tetrahedral molybdenum oxide species, which are supposed to lead to the very active catalyst centers. Furthermore, MoO<sub>3</sub>/MCM-41 with co-catalyst was also active in metathesis of functionalized alkenes (allylanisole, diethyl diallylmalonate).

Recently, new types of catalysts were prepared by direct incorporation of molybdate anions into MCM-41 during its synthesis. This catalyst with 1 wt. % of Mo exhibited 55 % conversion of 1-octene and 97 % selectivity to 7-tetradecene after 360 min of the reaction, which represents better specific activity than that of MoO<sub>3</sub>/MCM-41 catalysts. With the catalyst prepared by supporting MoO<sub>3</sub> on zeolite Beta (loading 4 wt. % of Mo) 80 % conversion of 1-octene but only 16 % selectivity to 7-tetradecene was reached after 360 min of the reaction.

The new systems based on molybdenum oxide and mesoporous molecular sieves represent inexpensive, easy-to-prepare and highly active and selective heterogeneous catalysts for metathesis of linear alkenes applicable under mild conditions without the necessity of solvent or co-catalyst presence in the reaction mixture.



## THE SPBS VERSUS GUVS – THE FINAL COUNTDOWN

**Anna Zan**

*Martin Hof*

The cellular membranes, forming a fluid structure of a broad spectrum of lipids and proteins, are crucial in maintaining the functions of living cells. The membranes create semi-permeable barriers that are responsible for the existence of ordered structures and compartments within cells. In recent years, there has been a great interest in the research concerning lipid membranes.

In order to avoid the complexity of bio-membranes, simplified, a range of model systems has been created and studied. The need of such studies results from the broad applications of lipid self-assemblies ranging from pharmacological vehicles to biosensors.

The Supported Phospholipid Bilayers (SPBs), are useful model systems for fluorescent measurements. The SPBs are formed by adsorption of lipid vesicles on the solid support. They provide regular and stable structure. On the other hand, the spherical lipid vesicles, also called liposomes, resemble cell membranes more closely. However, the only type of liposomes relevant to microscopic observations are the giant unilamellar vesicles (GUVs) having the diameter of up to 300 $\mu$ m.

The co-existence of SPB's and Giant Unilamellar Vesicles (GUVs ) has lasted for more than two decades. The question of constructing a bridge between the free-standing membranes and the supported lipid bilayer has, until now, remained unsolved.

Based on the lateral diffusion coefficient determined by the use of confocal FCS (*Benda A. et al. Langmuir 19(10), 4120, (2003)*) we present the comparison of supported phospholipid bilayers versus giant unilamellar vesicles. The diffusion of the free-suspended membranes of GUVs is approximately twice as faster as in the case of supported bilayers. Our results should make a step forward in the difficult task of comparing the research based on GUVs and SPBs.