Organic Chemistry **299**

Physical Chemistry **300**

Understanding the solvent effect in transfer along a hydrogen bonded wire.

Carine Manca[1], Christian Tanner[2], Markus Thut[2], Samuel Leutwyler[2]

[1] ETH Zürich, Laboratorium für Physikalische Chemie, ETH-Hönggerberg,
CH-8093 Zürich, Switzerland
[2] Departement für Chemie und Biochemie, Universität Bern,
CH-3000 Bern, Switzerland

We study small systems to reproduce and understand the basic properties of transfer observed along hydrogen bonded wires like transmembrane proteins which utilize proton gradients across biological membranes, or like aquaporins which provide a path for water molecules but prevent protons from crossing the cell membrane. In our study, a photoacid (7-hydroxyquinoline, 7HQ) with two functional H-donor and H-acceptor groups is used (i) as a scaffold molecule to control the length of the wire attached to, and (ii) as a probe for the transfer along the wire by the *enol* → *keto* tautomerization of 7HQ.

With help of *ab initio* calculations and spectroscopic measurements in molecular beam, we have been able to observe and explain an excited state H atom transfer (ESHAT) along a wire of three ammonia molecules with a vibrational excess of energy of 200 cm^{-1} [1], and to infirm any competition with an excited state proton transfer (ESPT) mechanism for this wire [2]. Surprisingly, substituting ammonia with water blocks the ESHAT along the wire, at least with a vibrational excess of energy of 1200 cm^{-1} [3]. This highlights the role of the solvent in transfers along these wires. We explain this solvent effect in terms of exo- and endoergic reaction and in terms of H atom affinity.

We also extend our model to wires with methanol, (di)methylamin and formic acid where the mechanism seems to be more complex and we present some predicted reaction paths.

[1] Ch. Tanner, C. Manca, S. Leutwyler *Science*, **2003**, *302*, 1736.
[2] ibid. *J. Chem. Phys.*, **2005**, *in press.*
[3] ibid. *Int. Rev. Phys. Chem.*, **2005**, *in preparation.*

Physical Chemistry **301**

Infrared spectroscopic study of gas-phase zwitterion formation: hydrated valine-Li^+ and valine-H^+

A. Kamariotis, S. Mercier, O. Boyarkin, R. Beck, M. Bush, E.R. Williams, T. R. Rizzo

Laboratoire de Chimie Physique Moleculaire, EPFL, CH-1015 Lausanne, Switzerland

In aqueous environment, amino acids exist as zwitterions with a protonated amino group and a deprotonated carboxylic acid, whereas in the absence of water they appear in their neutral form [1-2]. Efforts put in hydration studies explore the role of microsolvation in zwitterion stabilization[3], while the presence of another charge, either from the same molecule or an external ion may also stabilize zwitterion formation illustrating the role of salt bridges. BIRD experiments [4] have studied the combined effect of solvent and metal ion interactions, although they cannot unambiguously account for zwitterion formation.

Our approach is to investigate the relevant species by spectroscopy. Thus, we form water clusters of amino acids in an ion-trap tandem mass spectometer and use vibrational photo-fragmentation spectroscopy to probe the role of hydration and electrostatic forces on zwitterion formation.

This work presents results obtained for protonated and lithiated valine water clusters. By sequential hydration we seek to identify the number of water molecules necessary to stabilize the zwitterion in protonated valine and lithiated valine and how those compare.

[1] K. Iijima, Tanaka, K., Onuma, S., J. Mol. Struct., **1991**, 246, 257.
[2] S. G. Stepanian, I. D. Reva *et al.*, J Phys Chem A, **1998**, 102, 1041.
[3] P. Carcabal, R. Kroemer *et al.*, Phys. Chem. Chem. Phys. **2004,** 6, 4546.
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Physical Chemistry **302**

The heterogeneous chemical reaction of HOCl and HOBr with sea salt and model aerosols in an atmospheric flow tube reactor at 300K in the range 40 to 93% relative humidity

Pascal Pratte and Michel J. Rossi

Ecole Polytechnique Fédérale de Lausanne (EPFL), Laboratoire de Pollution Atmospheric et Sol (LPAS), 1015 Lausanne (Switzerland).

In the marine boundary layer inorganic chlorine and halogenated hydrocarbon gases were recently found in remote region [1]. The chemical conversion of alkali halide salts into volatile halogen-containing compounds that may be photolysed in the atmosphere is called halogen activation and is an active field of research. We present new results for HOCl and HOBr uptake on submicron acidified sea salt (SS) and NaCl aerosols in an atmospheric flow tube reactor. We observed that the acidity is necessary to enable heterogeneous reactions on SS and NaCl aerosols for both studied trace gases. Specifically, HOCl reacts only on acidified SS aerosols with a uptake coefficient ranging from 1.4 x 10^{-3} to 0.6 x 10^{-3} for rh between 70 and 90%, respectively, while HOBr reacts faster with both SS and NaCl. The uptake experiment of HOBr on SS, recrystallized SS or on NaCl aerosols were performed for rh ranging from 40 to 93%. A significant difference in the rate of uptake was found for acidified SS and NaCl aerosols as a function of rh:
of HOBr on acidified SS increases significantly at rh = 77% (= 8.4 x 10^{-3}) and decreases at higher rh in comparison to NaCl aerosols. In addition, we observed a difference in between acidified SS and NaCl by a factor of 2 and 10 for rh = 78 and rh = 90%, respectively. This difference in may perhaps be attributed to an organic phase forming a coating on the SS aerosol at high rh.

[1] Vogt, R.Crutzen, P. J. and Sander, R., Nature. **1996**, 383, 327.
[2] Abbatt, J. P. D and Waschewsky, G. C. G., Journal of Phys Chem A **1998,**102,3719.

Physical Chemistry **303**

Structures and Dynamics of Protonated Water Clusters

Antony Fouqueau, Markus Meuwly*

University of Basel, Department of Chemistry, Klingelbergstrasse 80, 4056 Basel

The structures and dynamics of protonated water clusters $H^+(H_2O)_n$ (n=2-8, 17, 21) are investigated by using DFT/B3LYP and *ab initio* Molecular Dynamics. For each cluster size, the different structural minima are calculated with the Self-Consistent Charges Density Functional Tight-Binding (SCC-DFTB) method and at the B3LYP/6-31G** level. Temperature effects are taken into account by performing SCC-DFTB/MD simulations at 50 and 100 K. The changes of structure are analysed from radial distribution functions. At lower temperature, the preferred structures are the ones presenting the less dangling H atoms forming a network structure. At higher temperatures, chain like structures are preferred and most of the isomers undergo an isomerisation which is reflected in a change of the infrared spectra and radial distribution function. The infrared spectra are discussed in view of recent experimental data[1]. It is found that for smaller cluster sizes predominantly one species contributes to the infrared spectrum while for larger cluster sizes several isomers are likely to be present.

[1] J.-W. Shin, N.I. Hammer, E.G. Diken, M.A. Johnson, R.S. Walters, T.D. Jaeger, M.A. Duncan, R.A. Christie & K.D. Jordan, *Science*, **2004**, *304*, 1137.

Physical Chemistry **304**

Ultrafast Dynamics of Fluorescent DNA Intercalators

Alexandre Fürstenberg[1], Marc Julliard[1], Todor G. Deligeorgiev[2], and Eric Vauthey[1]

[1]Department of Physical Chemistry, University of Geneva, 30 Quai Ernest-Ansermet, 1205 Genève, Switzerland, and [2]Faculty of Chemistry, University of Sofia, 1 James Bourchier Avenue, 1126 Sofia, Bulgaria

The synthesis of two dyes, YOYO and TOTO, which form extremely stable and highly fluorescent complexes with double-stranded DNA has been considered a breakthrough in the development of DNA probes for molecular biology. They are homodimeric derivatives of the cyanine dyes oxazole yellow (YO) and thiazole orange (TO). The interest for this class of dyes arose mainly from the fact that they display negligible fluorescence when free in solution and very strong fluorescence when bound to DNA, making them useful to detect DNA at sensitivity comparable to that of radioactive labels.

The extreme difference in quantum yield between the free and bound forms has been ascribed to the fact that rotation around the internuclear bridge between the benzoxazole, respectively benzothiazole and quinoline moieties, which allows for non-radiative relaxation of the free form, is hindered upon intercalation in DNA. This isomerization process, which governs the excited-state lifetime of the free dye in solution, was predicted to require less than 5 ps in water. We report here on femtosecond-resolved fluorescence measurements which confirm the occurrence of this process on a time-scale of a few picoseconds for YOYO-1 and other newly synthesized monomeric and dimeric YO and TO derivatives. Upon intercalation in DNA, the large amplitude motion of the fluorescent probes is strongly hindered and the excitonic coupling of two dimer subunits, which further reduces the fluorescence quantum yield of the free form, is disabled. Despite this, the decay of the fluorescence anisotropy was found to be ultrafast. This observation is an evidence of the occurrence of an ultrafast intramolecular excitation energy hopping between two dimer subunits intercalated in DNA.

Physical Chemistry **305**

Transient Electronic and Molecular Structure of Photoexcited Coordination Chemistry Compounds

W. Gawelda[1,2], V.T. Pham[1], M. Kaiser[1], Y. Zaushitsyn[1,2], R. Abela[2], M. Chergui[1] and C. Bressler[1]

[1]Laboratoire de Spectroscopie Ultrarapide LSU
Institut des Sciences et Ingénierie Chimiques ISIC
Ecole Polytechnique Fédérale de Lausanne EPFL
CH-1015, Lausanne, Switzerland
[2]Swiss Light Source, Paul Scherrer Institut
CH-5232 Villigen PSI, Switzerland

The understanding of the local geometric and electronic structure is a prerequisite to our knowledge about chemical reactivity. Consequently, in order to understand chemical reaction pathways including branching ratios to different possible products, one would seek to monitor the electronic and structural changes of an ongoing chemical reaction.

The X-Ray Absorption Fine Structure (XAFS) is an ideal tool to study local geometric structure (bond distances), while bound-bound transitions are sensitive to the local electronic structure including the geometrical symmetry of the studied molecule.

We have studied the triplet Metal-to-Ligand Charge Transfer (^{3}MLCT) states of ruthenium (II) tris (2,2')bipyridine, $[Ru^{II}(bpy)_3]^{2+}$, in aqueous solution. The photoexcitation promotes an electron is promoted from the Ru atom to one of the bpy ligands, and this should change the structure of this intermediate compound. $[Ru^{II}(bpy)_3]^{2+}$ is one of the most studied complex compounds in coordination chemistry, yet its excited state structure is not entirely understood. Hereby we probe the temporal evolution of the complex via XAS methods like EXAFS and XANES. Both methods show a measurable change between the ground state and the excited state structures. The results quantify the general feasibility of this novel technique, and model calculations are presented, which permit us to link the current results with possible structural distortions of the excited state of our model complex.

Physical Chemistry **306**

Photoionization Dynamics of Aqueous I⁻ in Water using Ultrafast Optical Pump-Probe and X-ray Absorption Spectroscopy

V. T. Pham[1], Y. Zaushitsyn[1], W. Gawelda[1], B. Sobanek[1], D. Grolimund[2], R. Abela[2], C. Bressler[1] and M. Chergui[1],

[1]Laboratoire de Spectroscopie Ultrarapide,
Ecole Fédérale Polytechnique de Lausanne,
CH-1015 Lausanne, Switzerland
[2]Swiss Light Source, Paul Scherrer Institute,
CH-5232 Villigen PSI, Switzerland

Electron photodetachment dynamics of 1 M/l aqueous iodide in water was investigated using a 266 nm excitation. Probing the transient absorption at the same wavelength show that I^- ions were bleached with a time constant of 260 fs (fig. 1), the decreasing of I^- ions are assigned to the creation of I atoms in the transient solvent. X-ray near-edge absorption structure (XANES) and extended x-ray absorption fine structure (EXAFS) were already investigated in the case of aqueous I^- [1]. These results and our optical measurements will be discussed in view of future picosecond time-resolved XAS experiments on the electron detachment from I^-.

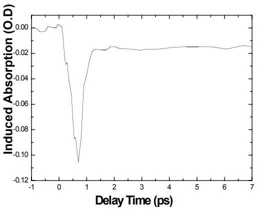

Fig.1 Time-resolved transient absorption of 1M/L I^- in water at 266 nm pumped by the same wavelength at 0.36 J/cm^2

[1] Ch. Bressler *et al*, *Journal Chemical Physics* **2002**, *116*, 2955.

Physical Chemistry **307**

A New VUV Laser System Producing Fourier-Transform-Limited Pulses of Arbitrary Shape and Duration for High-Resolution VUV Spectroscopy

T. A. Paul, R. Seiler and F. Merkt*

ETH Zürich, Laboratorium für Physikalische Chemie,
ETH-Hönggerberg, HCI, CH-8093 Zürich, Switzerland

A new, all-solid-state laser system has been developed which enables the generation of Fourier-transform-limited pulses of programmable shape and duration. The laser system is based on the pulse-amplification of the single-frequency near-infrared (NIR) radiation delivered by a commercial Ti:sapphire ring laser. The pulses are obtained from the continuous wave (cw) NIR ring laser output using the pulsed first order diffraction sideband of a freely programmable acousto-optic modulator and are pulse-amplified in Ti:sapphire crystals pumped by the 532 nm output of a Nd:YAG laser in a multipass arrangement. Pulse energies of up to 15 mJ, 1 mJ, 100 μJ and 1 nJ are generated in the NIR, visible, UV and VUV (vacuum ultraviolet) ranges, respectively. The tunable range of this pulsed laser can be extended from the NIR (720 - 825 nm) to the visible (360 - 412 nm) and the UV (240 - 275 nm) by frequency doubling and tripling in nonlinear crystals. The tunable range has also been extended to several regions of the VUV range between 66200 and 94000 cm^{-1} by resonance-enhanced sum- and difference-frequency mixing in xenon using the $(5p)^5 6p[1/2]_0 \leftarrow (5p)^6\ ^1S_0$ two-photon resonance at 80118.96 cm^{-1}. The characterization of the system, including the determination of frequency chirps and shifts, of pulse shapes in the various frequency ranges and of the bandwidth will be presented. A bandwidth of 120 MHz (corresponding to a resolving power $\frac{\nu}{\Delta\nu} = 3 \cdot 10^7$ at 93000 cm^{-1}, the best obtained so far in the VUV) has been achieved as measured by the FWHM of spectral lines.

Physical Chemistry **308**

Water Splitting with Sensitized AgCl Photoanodes

Vanga R. Reddy, A. Currao and G. Calzaferri

University of Bern, Department of Chemistry and Biochemistry,
Freiestrasse 3, 3012 Bern, Switzerland

We have reported that appropriately prepared silver chloride electrodes photocatalytically oxidize water to O_2 under suitable conditions. The nanostructured silver chloride layer acts as photocatalyst in the presence of a small excess of silver ions in solution. The photoactivity of AgCl extends from the UV into the visible light region due to self-sensitization, caused by the formation of silver species during the photoreaction [1].

We observed that small traces of Au colloids greatly influenced the photoelectrochemical activity of AgCl photoanodes. The O_2 production and the photocurrent were increased by a factor of about 3 [2]. To test its water splitting capability, AgCl photoanodes were combined with an amorphous silicon solar cell. The AgCl layer was employed in the anodic part of a setup for photoelectrochemical water splitting. A platinum electrode and an amorphous silicon solar cell were used in the cathodic part. Illumination of the AgCl photoanode and the amorphous Si solar cell led to photoelectrochemical water splitting to O_2 and H_2 [3]. We are also investigating the effect of zeolite A as a back support for the AgCl layer in photoelectrochemical water oxidation experiments. First results will also be presented.

[1] D. Schürch, A. Currao, S. Sarkar, G. Hodes, G. Calzaferri, *J. Phys. Chem. B* **2002**, *106*, 12764.
[2] A. Currao, V. R. Reddy, G. Calzaferri, *ChemPhysChem* **2004**, *5*, 720.
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Physical Chemistry **309**

Efficient Ionic Liquid Electrolytes for Mesoscopic Dye Sensitized Solar Cells

Daibin Kuang, Seigo Ito, Shaik M Zakeeruddin and Michael Grätzel

Laboratory for Photonics and Interfaces, Ecole Polytechnique Fédérale,
CH-1015 Lausanne, Switzerland

Nanocrystalline dye sensitized solar cells (DSC) are attracting considerable academic and industrial interest as low-cost, high efficiency alternatives to the conventional solid p-n junction photovoltaic devices. Encapsulation of volatile electrolyte is a critical issue in view of the practical applications. A viable solution to this problem is replacement of organic solvent electrolytes by ionic liquid electrolytes, whose vapor pressure is negligible. Ionic liquids with good chemical, thermal stability and wide electrochemical window have been recently pursued as alternative electrolytes for DSC.

Iodide based ionic liquids are viscous than conventional organic solvents. Binary ionic liquid electrolytes were prepared by mixing with low viscosity ionic liquids (having weakly coordinating anion) to reduce the viscosity of these electrolytes. A detailed investigation of these binary ionic liquid electrolytes for high performance of DSC revealed that an increase in the iodide diffusion flux is critical than its diffusion coefficient. This talk will summarize the most recent developments in the use of ionic liquid electrolytes for DSC.

[1] Peng Wang, Bernard Wenger, Robin Humphry-Baker, Jacques-E-Moser, Joel Teuscher, Willi Kantlehner, Jochen Mezger, Edmont V. Stoyanov, Shaik M. Zakeeruddin and Michael Grätzel. *J. Am. Chem. Soc* . **2005**, *127*, 6850.
[2] Peng Wang, Shaik M. Zakeeruddin, Robin Humphry-Baker and Michael Grätzel. *Chem. Mater* . **2004**, 16, 2694.

Physical Chemistry **310**

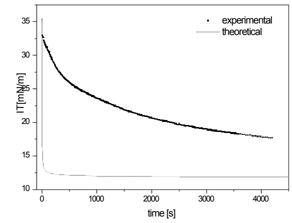
Kinetics of adsorption of the azacrown ether at liquid-liquid interface

K. Wojciechowski, J. Buffle

Analytical and Biophysical Environmental Chemistry (CABE)
Chimie Analytique Minérale et Applique, Sciences II
30 quai E. Ansermet, CH-1211 Genève 4, Suisse

The surface activity of the extracting agents has been attracting more and more attention due to a crucial role it may play in many fields of separation and analytical science. In this contribution we will present results of our mechanistic studies of the carrier-assisted ion transport through a liquid-liquid interface of Permeation Liquid Membrane (PLM).

Although chemical properties of crown ethers in bulk are quite well known, they might be much different at interfaces. The adsorption of the carrier used in the PLM transport experiments, an azacrown ether (1,10-didodecyl-1,10-diaza-18-crown-6) at toluene-water interface was investigated using dynamic interfacial tension measurements. Contrary to expectation the adsorption is very slow, few orders of magnitude slower than one would predict from the diffusion-limited adsorption using the Word-Tordai theory.



We show that the slow decay of interfacial tension does not originate from the presence of surface-active impurities, neither from a hydrolysis of the adsorbed molecules at the interface. The arguments for a kinetics-limited adsorption of the azacrown ether at liquid-liquid interface will be presented.

Physical Chemistry **311**

A New Paradigm in Molecular Engineering of Sensitizers for Solar Cell Applications

C. Klein, Md. K. Nazeeruddin, P. Liska, P. Comte and M. Grätzel

Laboratory for Photonics and Interfaces, Institute of Chemical Science and
Engineering, Ecole Polytechnique Fédérale de Lausanne,
CH-1015 Lausanne, Switzerland.

Novel ruthenium(II) complexes of the type [RuLL'$(NCS)_2$] (where L=4,4'-dicarboxy-2,2'-bipyridine; L' = 4,4'-di-(2-(4-hexyloxyphenyl)ethenyl)-2,2'-bipyridine or 4,4'-di-(2-(2,5-dimethoxyphenyl)ethenyl)-2,2'-bipyridine or 4,4'-di-(2-(2-methoxy-4-nonyloxyphenyl)ethenyl)-2,2'-bipyridine or 4,4'-di-(2-(2,4,6-trimethoxyphenyl)ethenyl)-2,2'-bipyridine) were synthesized and characterized by analytical, spectroscopic and electrochemical techniques. The absorption spectra of these sensitizers are dominated by metal to ligand charge transfer transitions (MLCT) in the visible region and with the lowest allowed MLCT bands appearing at 394 and 550 nm. The molar extinction coefficients of these bands are significantly higher than those of the standard sensitizer *cis*-dithiocyanatobis(4,4'-dicarboxylic acid-2,2'-bipyridine)Ruthenium(II), (N3). DFT and TDDFT studies of the electronic and optical properties of these sensitizers were performed. The calculated absorption spectra are in good agreement with the experimental data, and provide a detailed understanding of the charge transfer transitions. The calculations point out that the top three frontier filled orbitals have essentially ruthenium 4d (t_{2g} in octahedral group*)* character with sizable contribution coming from the NCS ligand orbitals. The photovoltaic data of these sensitizers adsorbed on TiO_2 films in a mono-protonated state, using an electrolyte containing 0.60 M 1-propyl-3-methylimidazolium iodide (PMII), 0.03 M I_2, 0.10 M guanidinium thiocyanate and 0.50 M *tert*-butylpyridine in a mixture of acetonitrile and valeronitrile (volume ratio: 85:15), exhibited a short circuit photocurrent density of 17.50 ± 0.20 mA/cm^2, the open circuit voltage was 790 ± 30 mV and a fill factor of 0.72 ± 0.03, corresponding to an overall conversion efficiency of 10.0% under standard AM 1.5 sunlight.

Physical Chemistry **312**

In situ spectroscopic studies in supercritical carbon dioxide: Selective oxidation of benzyl alcohol on Pd/Al_2O_3 as model reaction

Jan-Dierk Grunwaldt, Matteo Caravati, Alfons Baiker

Department of Chemistry and Applied Biosciences, Swiss Federal Institute
of Technology, ETH Hönggerberg, CH-8093 Zürich

The use of supercritical carbon dioxide ($scCO_2$) as solvent is attractive in catalysis for several reasons: $scCO_2$ exhibits fair and tunable solvent power especially for unpolar compounds and is completely miscible with gases. In addition, it can be regarded as a "green" solvent. The chemical inertness of CO_2 renders it particularly interesting for partial oxidation reactions with molecular oxygen. Despite a number of reactions perform better in supercritical fluids, hardly any *in situ* spectroscopic studies have been reported which could give a deeper understanding and provide rational criteria for better exploitation of SCFs in heterogeneous catalysis [1].

The Pd-catalysed benzyl alcohol oxidation with molecular oxygen is a well-suited model reaction since the reaction rate in $scCO_2$ is significantly higher than in conventional fluids [2]. Hence, we investigated the reaction by *in situ* spectroscopy at pressures up to 150 bar. For this purpose, the phase behaviour was identified by *in situ* monitoring using a view cell combined with transmission infrared and ATR-IR spectroscopy [3]. In addition, we applied *in situ* infrared spectroscopy for following the reaction progress while investigating simultaneously the solid/fluid interface. Finally, we report the first *in situ* EXAFS study of a heterogeneous catalyst in a SCF, giving insight into the oxidation state of the palladium constituent under reaction conditions. The results evidence that single phase conditions are beneficial for the reaction and the reaction rate increases with increasing oxygen partial pressure. However, a too high oxygen partial pressure leads to surface oxidation of the Pd-particles resulting in catalyst deactivation.

[1] J.-D. Grunwaldt, R. Wandeler, A. Baiker, Catal. Rev. Sci. Eng. **2003**, *45*, 1.
[2] M. Caravati, J.-D. Grunwaldt, A. Baiker, Catal. Today **2004**, *91-92*, 5.
[3] M. Caravati, et al. Phys. Chem. Chem. Phys. **2004**, *7*, 278.

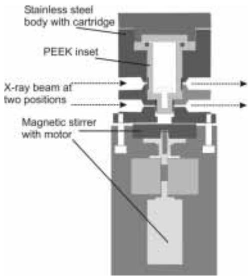
Physical Chemistry **313**

In situ EXAFS study concerning the hydrothermal transformation of $MoO_3 \cdot 2H_2O$ to MoO_3 nanorods

Jan-Dierk Grunwaldt, Alexej Michailovski, Alfons Baiker, Greta R. Patzke

Department of Chemistry and Applied Biosciences, Swiss Federal Institute of Technology, ETH Hönggerberg, 8093 Zürich, Switzerland

High pressure reactions that involve both liquid and solid phases are encountered in various areas of chemistry, including the synthesis of inorganic materials and heterogeneous catalysis. An interesting hydrothermal transformation is the preparation of MoO_3 nanorods from $MoO_3 \cdot 2H_2O$ [1]. The formation of submicrometer fibres of MoO_3 proceeds in both neutral ionic and acidic media at 90 - 180°C within several hours to several days. The XANES and EXAFS spectra of $MoO_3 \cdot 2H_2O$ and MoO_3 are different due to the change in the local structure. Hence, the technique was used to uncover whether a topotactic transformation $MoO_3 \cdot 2H_2O \rightarrow \beta\text{-}MoO_3 \cdot H_2O \rightarrow MoO_3$ occurs or whether soluble Mo species form during the transformation. This requires *in situ* spectroscopic studies so that the transformation was studied with a new spectroscopic batch reactor cell for EXAFS with two different pathlengths and path positions (see Figure). Structural changes in the solid material (formation of MoO_3 from $MoO_3 \cdot 2H_2O$) were detected as soon as the first soluble species were observed in solution. This indicates that the formation of MoO_3 rods from $MoO_3 \cdot 2H_2O$ proceeds via soluble Mo species rather than following a topotactic transformation. This is further substantiated by laboratory experiments and *in situ* X-ray diffraction data [2].



[1] G. R. Patzke, A. Michailowski, F. Krumeich, R. Nesper, J.-D. Grunwaldt, A. Baiker, *Chem. Mater.* **2004**, *16***,** 1126.
[2] A. Michailowski, J.-D. Grunwaldt, A. Baiker, R. Kiebach, W. Bensch, G. R. Patzke, *Angew. Chem.*, submitted.

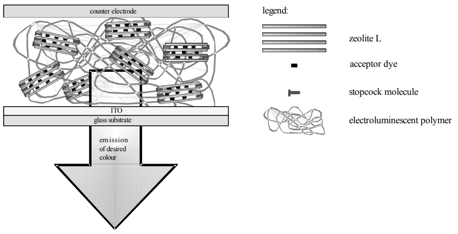
Physical Chemistry **314**

Dye Loaded Zeolite L Antenna Materials for Organic Light Emitting Diodes

Olivia Bossart, Gion Calzaferri

University of Berne, Freiestr. 3, CH-3012 Berne, Switzerland

The combination of semi conducting polymers and dye loaded zeolite L crystals in organic light emitting diodes (OLED) allows an easy way of tuning the emission colour of LEDs. Electronic excitation energy is transferred from the electrically excited polymer onto stopcock molecules at the entrances of the zeolite L channels and from there onto dyes which are incorporated inside the channels. By using different dyes inside the zeolites and varying the dye ratios it is possible to span the visible spectrum and even have NIR emitting LEDs. The insertion of the acceptor dyes into zeolite L channels provides a stable material with a high monomeric dye concentration reaching up to 0.4 mol/L.



[1] G. Calzaferri et al., *Angew. Chem. Int. Ed.* **2003**, 42, 3732.

Physical Chemistry **315**

Slow Diffusion by Singlet State NMR

Simone Cavadini[§], Jens Dittmer[£], Sasa Antonijevic[§] and Geoffrey Bodenhausen[§$]

[§]EPFL, SB-ISIC-BCH, 1015 Lausanne, Switzerland
[$] Ecole Normale Supérieure, 24 rue Lhomond, 75231 Paris cedex 05, France
[£] Aarhus University, Langelandsgade 140, 8000 Aarhus C, Denmark

Nuclear magnetic resonance (NMR) has long been known as a flexible tool to study transport phenomena such as diffusion, flow, convection, or electrophoretic mobility. The information about the localization of the molecules can be encoded and decoded by pulsed field gradient (PFG) before and after a delay (Δ) where translation motion can occur. Slow diffusion measurements require big delays Δ which are limited by the longitudinal relaxation time T_1. Recently, Carravetta et al. [1] have shown that the nuclear spin order can be stored as *singlet states* which relax with a time constant T_s that can be an order of magnitude longer than T_1. Here we utilize these longer living states in order to measure smaller diffusion rates than PFG-NMR techniques.

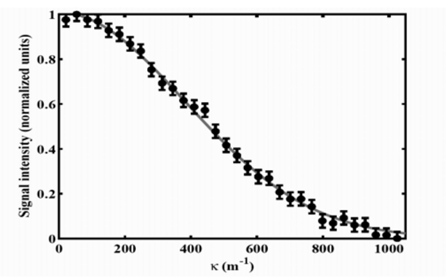


Figure 1. Signal decay as a function of the pulse field gradient

[1] Carravetta, M.; Levitt, M. H.; *J. Am. Chem. Soc.*, **2004**, *126*, 6228

Physical Chemistry **316**

State-resolved gas/surface reactivity of methane in the symmetric C-H stretch vibration on Ni(100)

Plinio Maroni, Dimitrios C. Papageorgopoulos, Marco Sacchi, Than T. Dang, Rainer D. Beck, and Thomas R. Rizzo

Ecole Polytechnique Fédérale de Lausanne,
Laboratoire de Chimie Physique Moléculaire
1015 Lausanne

The state resolved reactivity of CH_4 in its totally symmetric C-H stretch vibration (ν_1) has been measured on a Ni(100) surface. Methane molecules were accelerated to kinetic energies of 49 and 63.5 kJ/mol in a molecular beam and vibrationally excited to ν_1 by stimulated Raman pumping before surface impact at normal incidence. The reactivity of the symmetric-stretch excited CH_4 is about an order of magnitude higher than that of methane excited to the antisymmetric stretch (ν_3) reported by Juurlink et al. [Phys. Rev. Lett. **83**, 4 (1999)] and is similar to that we have previously observed for the excitation of the first overtone ($2\,\nu_3$). The difference between the state resolved reactivity for ν_1 and ν_3 is consistent with predictions of a vibrationally adiabatic model of the methane reaction dynamics and indicates that statistical models cannot correctly describe the chemisorption of CH_4 on nickel.

Physical Chemistry **317**

Ultrafast Solvation at Water/ZrO_2 Interface

E. Portuondo-Campa*, A. Tortschanoff*, F. van Mourik*, J-E. Moser[&],
A. Kornherr[$], M. Chergui*

* Laboratoire de Spectroscopie Ultrarapide, ISIC, Ecole Polytechnique
Fédérale de Lausanne. CH-1015 Lausanne, Switzerland
[&] Laboratoire de Photonique et Interfaces, ISIC, Ecole Polytechnique
Fédérale de Lausanne. CH-1015 Lausanne, Switzerland
[$] Institute of Physical Chemistry, University of Vienna, Währingerstr. 42,
A-1090 Wien, Austria

Due to the special importance of Ti in biomedical applications there is great interest in the investigation of the structure and dynamics of water close to Me(IV)-oxide surfaces. Dyes attached to the surface of ZrO_2 nanoparticles in colloidal solution can be used as probes for the ultrafast rearrangement of the surrounding water molecules upon excitation of the dyes.

We performed ultrafast transient absorption and photon echo techniques to study solvation dynamics around dyes in bulk and interfacial water. Our results reproduce the typical time scales and non-exponential behavior of the solvation process in water, but show only subtle differences between bulk and interface, contrary to what one would expect from the altered ordering of the solvent at the surface.

Molecular dynamics simulations suggest that the interface region is limited to no more than one or two water layers, while the dye molecule extends over ~10 Å, such that most of it is immersed in bulk-like water. In this scenario, dye – based techniques prove to be insufficient for establishing the dynamic properties of the interface. As an alternative, we propose a Transient Optical Kerr Effect (OKE) experiment, presently running in our lab, which directly probes the rotational diffusion of the water molecules without need for a probe dye. First results for this technique will also be presented.

Physical Chemistry **318**

Photoelectron Spectroscopy of Aromatic Molecules Embedded in Liquid Helium Nanodroplets

Marcel Drabbels and Evgeniy Loginov

Laboratoire de Chimie Physique Moléculaire, École Polytechnique Fédérale
de Lausanne, CH-1015 Lausanne, Switzerland

Photoionization and photoelectron spectroscopy of aniline embedded in liquid helium nanodroplets (HeD) has been performed. The aim of this work is to understand the mechanism of photoionization in nanodroplets and the interaction between the created photoelectron and the He atoms in the droplet. The insight into these processes will forward further experiments on molecular species that cannot be created or investigated in conventional beam techniques. Aniline molecules are ionized by 1+1 and 1+1'resonance enhanced multi-photon ionization (REMPI) via the $S_1 \leftarrow S_0$ transition. The REMPI spectrum of aniline in HeD is found to resemble that of gas phase but with blue-shifted and broadened lines due to the interaction of the solvated molecule with helium environment and the large geometrical changes in the molecule upon the excitation. Photoelectron imaging is used to characterize the angular and the kinetic energy distributions of the escaped photoelectrons from the HeD. Compared to the gas phase the photoelectron spectra are shifted to the higher photoelectron kinetic energies and the peaks are asymmetric towards lower energy. The shift of the photoelectron energy is due to the lowering of the ionization potential upon solvation in helium. The asymmetry can be attributed to the energy transfer from the electron to the helium environment during the escape process.

Physical Chemistry **319**

Electronic spin relaxation mechanism study of acyclic and macrocyclic Gd(III) complexes based MRI contrast agents: multi-frequency and multi-temperature EPR approach

Meriem Benmelouka, Alain Borel, Lothar Helm, Andre.E Merbach[*]

Laboratoire de Chimie Inorganique et Bioinorganique, Ecole Polytechnique
Fédérale de Lausanne, EPFL-BCH, CH-1015 Lausanne, Switzerland

Gd(III) complexes are important as contrast agents that are used in Medical Magnetic Resonance Imaging[1]. The effectiveness *(relaxivity)* of the S-sate ion species as relaxation agents depends on a variety of factors including the rotational correlation time of the complex, the proton exchange rate and the electron spin relaxation rate. The Electron Paramagnetic Resonance provides a convenient characterization of the electron spin relaxation rate, which can be the factor limiting the *relaxivity* once the two first factors are optimized.

The basic theory of the EPR lineshape of Gd(III) complexes in solution[2] used the modulation of the transient Zero Field Splitting as the main relaxation mechanism. Recently, an improved model[3], where the electron spin relaxation is due to the combination of a static and dynamic Zero Field Splitting, has been developed.

We report here an EPR study for several Gd(III) complexes: $[Gd(TETA)]^-$, $[Gd(TRITA)(H_2O)]^-$, $[Gd(EPTPA)(H_2O)]^{2-}$. Multifrequency (9.4, 34, 75,150 and 225GHz) measurements were performed to get detailed information about the dynamics and the structure influence for each system. The new theoretical improved model has been used to analyze all the data.

[1] R.B. Lauffer, *Chemical Reviews.* **(1987)**, *87(5)*, 901-927.
[2] A. Husdon, J.W.E. Lewis, *Trans. Faraday Soc*. **(1970)**, *66*, 1297.
[3] S. Rast, A. Borel, L. Helm, E. Belorizky, P.H. Fries, A.E. Merbach, *Journal of the American Chemical Society.* (**2001**), *123(11)*, 2637-2644.

Physical Chemistry **320**

Molecular structure of $CuCl_2.2D_2O$ solid determined by two-dimensional ^2H NMR spectroscopy

Sasa Antonijevic and Geoffrey Bodenhausen

Ecole Polytechnique Fédérale Lausanne, Institut des Sciences et Ingénierie
Chimiques, BCH, CH-1015 Lausanne, Switzerland

A recently proposed two-dimensional ^2H NMR experiment [1] is implemented to study quadrupolar (Q) and paramagnetic shift anisotropy (PSA) interactions in powdered solid $CuCl_2{\cdot}2D_2O$. The spectra display motionally averaged lineshapes arising from time-dependent modulations of both interactions caused by 180° reorientational jumps of the water molecules around their DOD bisectors. An analytical method is developed to obtain the following parameters with high accuracy: the principal components of the two tensors (C_Q, η_Q, δ_{PSA}, η_{PSA}, δ_{iso}) and the Euler angles (α_Q, β_Q, γ_Q, α_{PSA}, β_{PSA}, γ_{PSA}) defining the relative orientations of the tensors with respect to the molecular frame. These parameters are than used to obtain information on the geometry of $CuCl_2.2D_2O$.

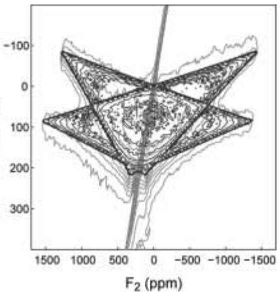


Figure 1. Experimental (green) and simulated (blue) two-dimensional ^2H NMR spectra (ν_0 = 61.4 MHz) of $CuCl_2{\cdot}2D_2O$ at 297 K. Assuming axial symmetry of both tensors ($\eta_Q = \eta_{PSA}$ = 0), the quadrupolar and PSA parameters are found to be $\alpha_Q = 0°$, $\beta_Q = 56.2°$, γ_Q = 0°, C_Q = 218.5 kHz, α_{PSA} = 0°, β_{PSA} = 37.0°, γ_{PSA} = 0°, δ_{PSA} = 310.2 ppm, and δ_{iso} = 74.7 ppm.

[1] S. Antonijevic and S. Wimperis, *J. Chem. Phys.* **2005**, *122*, 044312.

Physical Chemistry **321**

Monodirectional Antenna Systems

Arantzazu Zabala Ruiz, Huanrong Li, Gion Calzaferri

University of Berne, Freiestr. 3, CH-3012 Berne, Switzerland

In monodirectional antenna systems the harvested energy is transported in only one direction. Transport of electronic excitation energy through dye molecules inside the channels of zeolite L crystals occurs preferentially along the c-axis [1]. Oriented zeolite L monolayers, i.e., an arrangement consisting of zeolite L crystals oriented with their c-axis perpendicular to a substrate, is thus desirable for efficient transport of electronic excitation energy. Zeolite L crystals of low aspect ratio lead to oriented monolayers upon deposition onto a substrate. The successful assembly of oriented zeolite L monolayers largely depends on the ability to obtain zeolite L crystals with narrow size distribution and well-defined morphology [2]. We report successful results on the monolayer assembly of zeolite L crystals. We also show how we form the desired photonic monodirectional antenna by inserting dyes as indicated in figure 1.

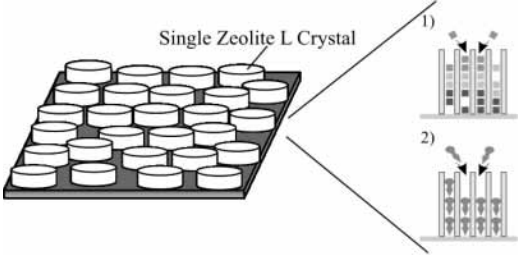


Figure 1: A monodirectional antenna system by 1) consecutively inserting dyes into a fixed zeolite, 2) insertion of a non-centrosymmetric dye entering the channels always with the same orientation leading to NLO materials.

[1] G. Calzaferri et al., *Angew. Chem.* **2003**, *42*, 3732.
[2] A. Zabala Ruiz et al., *Monatsh. Chem.* **2005**, *136*, 77.

Physical Chemistry **322**

Combined ATR–IR, DRIFT and TPO study of the effect of acetic acid on ethyl pyruvate adsorption onto Pt/Al_2O_3

Davide Ferri, Simon Diezi, Marek Maciejewski and Alfons Baiker

Department of Chemistry and Applied Biosciences, Swiss Federal Institute of Technology, ETH Hönggerberg HCI, 8093 – Zurich, Switzerland

Beside hydrogenation, ethyl pyruvate (EP) can undergo undesired side reactions on platinum [1,2] which might poison the catalyst surface under particular conditions. *In situ* ATR–IR spectra of EP solutions (1 mM, CH_2Cl_2) in contact with a model Pt/Al_2O_3 film show that at low hydrogen concentration EP decomposes on the metal to CO and hydrocarbon fragments. In addition to decarbonylation, EP polymerizes on a Pt/Al_2O_3 particulate film *via* aldol reaction on Al_2O_3 after hydrolysis of the ester group both processes occurring on base sites. A complex feature at around 1740 cm^{-1} and a band at 1659 cm^{-1} indicate the presence of multiple C=O and C=C groups. The *in situ* treatment of the catalyst surface with increasing concentration of acetic acid (0.1 to 10 mM, CH_2Cl_2) strongly inhibits EP polymerization. At the highest acetic acid concentration simulating solvent conditions the reaction was almost completely suppressed. *Ex situ* DRIFT spectra of catalysts after reactions (1 bar H_2, 10°C, CH_2Cl_2) mimicking the conditions in the ATR cell indicate that the processes observed by means of ATR–IR spectroscopy occur also during standard catalytic runs. Temperature programmed oxidation experiments on the samples revealed the presence of up to 3 wt% carbon deposit which decreased with increasing acetic acid concentration in solution.

The results indicate that ethyl pyruvate can undergo side reactions under conditions of enantioselective hydrogenation on Pt/Al_2O_3 leading to undesired adsorbed species and that the high enantiomeric excess obtained in acetic acid solvent may be attributable to suppression of these side reactions.

[1] D. Ferri, T. Bürgi, A. Baiker, *J. Phys. Chem. B* **2004**, *108*, 14384.
[2] E. Toukoniitty, D.Y. Murzin, *Catal. Lett.* **2004**, *93*, 171.

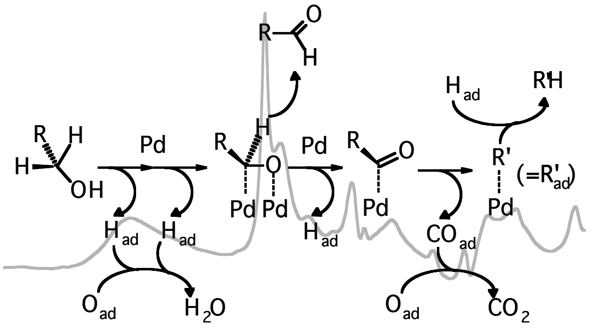
Physical Chemistry **323**

Monitoring of Surface Processes during Palladium-Catalyzed Alcohol Oxidation using ATR–IR Spectroscopy

Csilla Keresszegi, Davide Ferri, Tamas Mallat, and Alfons Baiker

Department of Chemistry and Applied Biosciences, Swiss Federal Institute of Technology, ETH Hönggerberg, CH – 8093 Zurich, Switzerland

Dehydrogenation and oxidative dehydrogenation[1] of six different primary and secondary, aliphatic and aromatic alcohols to carbonyl compounds have been studied by attenuated total reflection infrared (ATR–IR) spectroscopy combined with GC analysis. The studies revealed that all aldehyde products decarbonylated on Pd while the ketones were stable. Decarbonylation, and the hydrogenation type side reactions even in the presence of oxygen, support the validity of the classical dehydrogenation mechanism of alcohol oxidation. Furthermore, in the oxidation of primary alcohols the major role of oxygen is to remove the aldehyde degradation products (*i.e.* CO and the hydrocarbon fragments) and thus liberate free surface sites for alcohol dehydrogenation.



[1] Mallat, T. and Baiker, A., *Chem. Rev.*, **2004**, *104,* 3037.

Physical Chemistry **324**

Dissociative Electron Attachment to D-Ribose in the Gas Phase

Ilko Bald, Tomáš Skalický and Eugen Illenberger

Institut für Chemie, Physikalische und Theoretische Chemie, Freie Universität Berlin, Takustr. 3, 14195 Berlin, Germany

We have used the dissociative electron attachment (DEA) to D-Ribose (the backbone of RNA) to characterize its negative ion states. DEA to D-Ribose in the gas phase (the isolated molecule exists as a six-membered ring [1]) leads to the formation of many fragments near 0 eV (e.g. $[M–2H]^-$, $[M–H_2O]^-$, $C_3H_3O_2^-$, $C_3H_7O^-$, OH^-, and H^-). A peak near 0 eV with its shoulder at about 0.5 eV and a broad band peaking at around 7 eV were observed (Fig. 1). The 7 eV band can be ascribed to a core excited resonance.

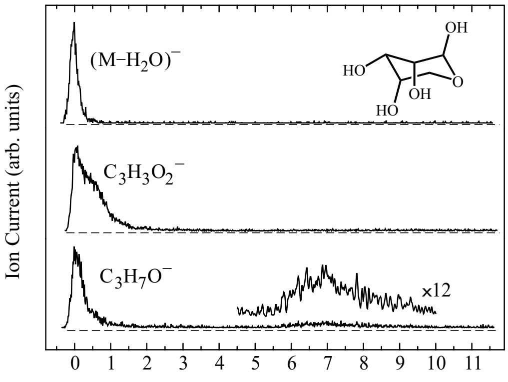


Figure 1 Comparison of selected ion yields resulting from DEA to D-Ribose.

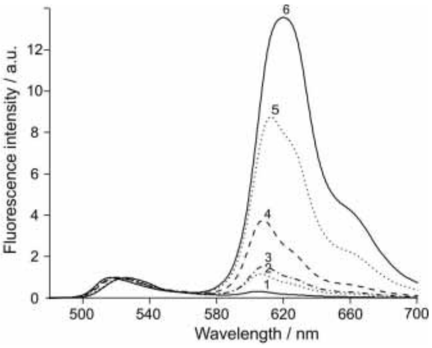
[1] L. P. Guler *et al.*, *J. Chem. Phys. A.* **2002**, *106*, 6754-6764.

Physical Chemistry **325**

A very elegant Förster energy transfer experiment

Katsiaryna Lutkouskaya and Gion Calzaferri

Department of Chemistry and Biochemistry, University of Bern,
Freiestr. 3, 3012 Bern, Switzerland



We investigated a series of samples were the ratio of the number of donor and acceptor molecules is constant (1:1) but their mean distance is decreasing. To achieve this over a large concentration range and to prevent concentration quenching, donor (pyronine) and acceptor (oxonine) molecules were included into zeolite L [1].

Dyes are randomly distributed inside of the channels of zeolite L. By selectively exciting pyronine at 460 nm, bands from both dyes can be observed, as illustrated in the Figure. The donor-acceptor distance decreases from 1 to 6 whereas the emission intensity of the acceptor increases. This means that energy transfer from pyronine (emission at 520 nm) to oxonine (emission at 610 nm) takes place. Time resolved measurements proved this. The rise of the acceptor luminescence is observed in samples with sufficiently large donor-acceptor distance. The donor luminescence follows a stretched-exponential model. – The shift of the emission maximum of the donor and of the acceptor at high loadings (5 and 6) is due to self-absorption.

[1] G. Calzaferri, S. Huber, H. Maas, C. Minkowski, *Angew. Chem. Int. Ed.* **2003**, *42*, 3732.

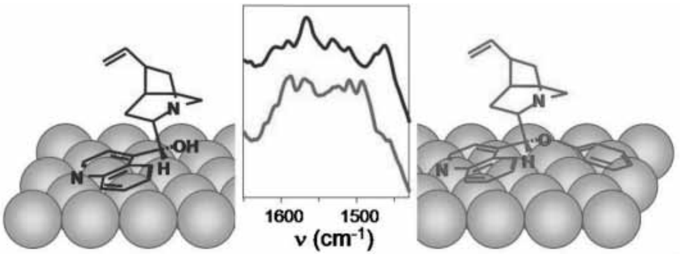
Physical Chemistry **326**

Switching of Enantioselectivity at Chiral Metal Surfaces

N. Bonalumi, A. Vargas, D. Ferri, T. Bürgi, T. Mallat, and A. Baiker

Department of Chemistry and Applied Biosciences
ETH-Hönggerberg, CH-8093 Zürich, Switzerland

The enantioselective properties of cinchona-modified platinum can be switched during heterogeneous enantioselective hydrogenations of activated ketones using chiral surface modifiers exhibiting different adsorption characteristics (geometry and strength). Structural studies on chirally modified metal surfaces have been performed by means of *in-situ* ATR-IR spectroscopy and DFT calculations in order to gain insight into the mechanism of this fascinating process [1]. The chiral modification of Pt upon adsorption and the competition for adsorption onto the metal surface between cinchonidine and its *O*-phenyl derivative were studied in the presence of CH_2Cl_2 solvent and H_2. DFT modeling supported the experimental results and provided submolecular information on the chiral space created by the adsorption of the chiral modifier on the metal.



[1] N. Bonalumi, A. Vargas, D. Ferri, T. Bürgi, T. Mallat, and A. Baiker, *J. Am. Chem. Soc.* in press.

Physical Chemistry **327**

The effect of gold on the adsorption properties of Pt and Pd model catalysts: An *in situ* ATR-IR study

Bahar Behzadi [ab], Davide Ferri [a], Karl-Heinz Ernst[b] and Alfons Baiker [a]

[a] Department of Chemistry and Applied Biosciences, Swiss Federal Institute of Technology, ETH Hönggerberg, CH – 8093 Zurich, Switzerland
[b] Molecular Surface Technologies, Swiss Federal Laboratories for Materials Testing and Research (EMPA), Ueberlandstrasse 129, CH – 8600, Dübendorf, Switzerland

The formation of alloy in bimetallic catalysis often causes remarkable alterations in activity and selectivity which can reflect the changed adsorption properties of the catalyst. The influence of gold on the adsorption of CO and cinchonidine (CD) from CH_2Cl_2 solvent at 283 K on Pd, Pd/Au, Pt and Pt/Au films was investigated using Attenuated Total Reflection Infrared (ATR-IR) spectroscopy. The model catalysts were prepared by electron beam deposition of 0.2–2 nm Pt and Pd on 1 nm Au on a Ge internal reflection element [1]. In the case of CO adsorption, the intensity of the CO signal was attenuated in the presence of gold in comparison to neat metal films. No CO adsorption was detected for Pd films thinner than 0.5 nm. On the contrary, CO signals could be observed on all Pt films. CO adsorption revealed a powerful tool to demonstrate alloying, which appeared more favoured for the Pd-Au pair. In the case of CD, the presence of gold facilitated the tilted adsorption of CD. Interestingly, the contribution from π-bonded species clearly vanished at decreasing Pt thickness. Only N–lone pair bonded species were detected on Pd, whose amount decreased with Pd content. On Au only, CD exhibited a single band at 1509 cm^{-1} suggesting formation of strongly oriented CD films. The effect of alloying supports the assignment of the ATR signals made for flat and tilted adsorbed CD [2]. Moreover, metal alloying more likely reduces the amount of surface sites available for adsorption by diluting the size of Pt and Pd ensembles on gold.

[1] D. Ferri, T. Bürgi, A. Baiker, *J. Phys. Chem. B* **2004**, *108*, 14384.
[2] D. Ferri, T. Bürgi, *J. Am. Chem. Soc.* **2001**, *123*, 12074.

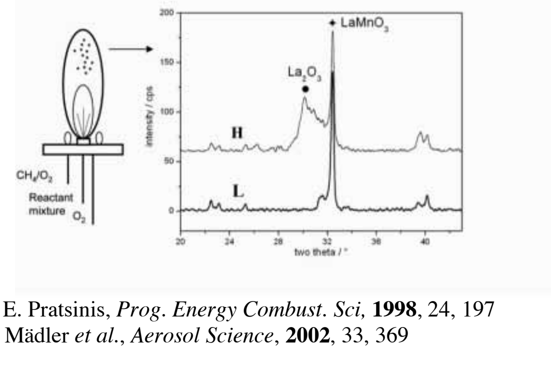
Physical Chemistry **328**

Flame Spray Pyrolysis – Application in perovskite phase-tuneability

N. van Vegten, M. Maciejewski, D. Ferri, A. Baiker

Department of Chemistry and Applied Biosciences, Swiss Federal Institute of Technology, ETH Hönggerberg, CH-8093 Zürich

Aerosol processes have been applied for many years in synthesis of a wide variety of single and multi-component metal (oxide) materials with applications such as pigments, solid oxide fuel cells, membranes, and catalysts [1]. Among the several aerosol synthesis techniques, flame spray pyrolysis (FSP) [2] has proven to be a very versatile and robust preparation method. In this contribution, FSP synthesis of $LaMnO_3$ will be discussed. Solutions of lanthanum and manganese complexes in a methanol/acetic acid mixture are sprayed into an oxygen/methane flame. In the flame, perovskite formation takes place and the material is collected on a cooled filter. It will be shown that by changing the flame temperature the composition of the products can be tuned, ranging from pure perovskite to its mixture with lanthana. The study includes investigation of the influence of parameters as such precursor concentration on the yield of perovskite formation and its properties.



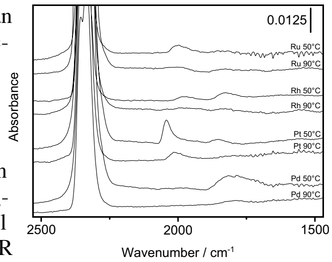
[1] S. E. Pratsinis, *Prog. Energy Combust. Sci,* **1998**, 24, 197
[2] L. Mädler *et al.*, *Aerosol Science*, **2002**, 33, 369

Physical Chemistry **329**

Supercritical CO_2 – An inert solvent for catalytic hydrogenation?

Marco Burgener, Davide Ferri, Jan-Dierk Grunwaldt, Tamas Mallat, and Alfons Baiker

Department of Chemistry and Applied Biosciences, Swiss Federal Institute of Technology, ETH Hönggerberg, CH-8093 Zurich, Switzerland



Supercritical carbon dioxide is an attractive solvent in hydrogenation reactions over solid catalysts. However, CO_2 may react on the surface of Pt-group metal particles with H_2 leading to poisonous CO. Therefore, surface species originating from the reaction between CO_2 and H_2 over Al_2O_3-supported Pt, Pd, Rh, and Ru model catalysts were investigated by ATR-IR spectroscopy under high pressure conditions. A batch reactor equipped with ATR-crystal and transmission IR windows and a continuous-flow cell with an internal reflection element were used. The study evidenced that CO formation from dense CO_2 in the presence of hydrogen is a feasible reaction over all Pt-group metals commonly used in heterogeneous catalytic hydrogenations in “supercritical” CO_2. In the batch reactor cell formation of CO was detected on all metals at 50 and 90°C, with the highest rate on Pt (see Fig.). Additional surface species were observed on Pt/Al_2O_3 at 150 bar under static conditions. In the continuous-flow cell, CO formation on Pt/Al_2O_3 was less extensive than in the batch reactor cell. From the studies we conclude that CO formation in CO_2-H_2 mixtures remains a minor side reaction during hydrogenation reactions on Pt-group metal catalysts and dense (“supercritical”) CO_2 may be considered as an essentially inert solvent for practical applications. Still, in some cases even small amounts of CO adsorbed on specific surface sites can affect a structure sensitive hydrogenation reaction and may be the origin of unexpected shifts in the product distribution.

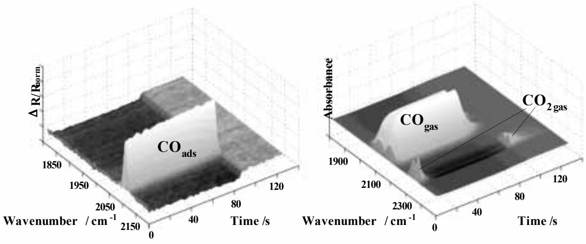
Physical Chemistry **330**

Polarization-Modulation Infrared Reflection-Absorption Modulation Excitation Spectroscopy: A new possibility for simultaneous monitoring surface/gas species and properties

Atsushi Urakawa, Thomas Bürgi[†], and Alfons Baiker

Department of Chemistry and Applied Biosciences, Swiss Federal Institute of Technology, ETH-Hönggerberg, CH-8093 Zürich, Switzerland, [†]U. Neuchâtel

Polarization-Modulation Infrared Reflection-Absorption Spectroscopy (PM-IRRAS) is a sensitive tool in the analysis of species residing at gas-solid and gas-liquid interfaces. The polarization-modulation allows excellent background compensation, and the analysis of surface/interface species under moderate pressure (e.g. atmospheric pressure of IR-absorbing gases) is possible. We demonstrate a new possibility to extract information of gas and solid phases in addition to surface species from the PM-IRRAS experiments, using CO oxidation over Pt film as an example. Modulation Excitation Spectroscopy has been combined with the technique to enhance the sensitivity. The surface species involved in the oxidation process, the state of Pt, and the gas phase species (CO and CO_2) could be simultaneously monitored and analyzed qualitatively and quantitatively.



Physical Chemistry **331**

Mechanistic aspects of aerobic oxidations catalyzed by promoted Ru-hydroxyapatite

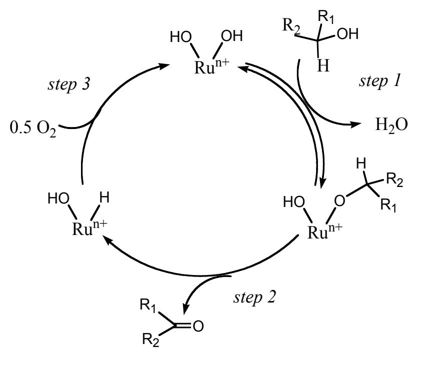
Zsuzsanna Opre, Jan-Dierk Grunwaldt, Tamas Mallat and Alfons Baiker

Department for Chemistry and Applied Biosciences, Swiss Federal Institute of Technology, ETH Hönggerberg HCI, CH-8093 Zurich, Switzerland.

Aerobic oxidation of alcohols to aldehydes and ketones over solid catalysts is an important transformation in “green” chemistry.

The RuCoHAp catalyst was prepared by ion exchange of hydroxyapatite (HAp) with $CoCl_2$ and $RuCl_3$. The high activity and selectivity of RuCoHAp in the aerobic oxidation of alcohols is attributed to isolated Ru hydroxo species in the apatite matrix.

Hammett correlation studies, primary kinetic isotope effect and in situ EXAFS measurement indicate the involvement of a ruthenium alcoholate species and β-hydride elimination from the alcoholate followed by the re-oxidation of the catalyst (see below), where the rate determining step strongly depends on the relative speed of the dehydrogenation of the Ru-alcoholate species and the reoxidation of Ru-hydride species.

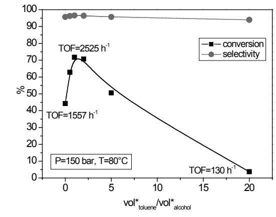


Physical Chemistry **332**

Tuning supercritical fluids by co-solvents: a remarkable increase of the benzyl alcohol oxidation rate by addition of toluene

Matteo Caravati, Jan-Dierk Grunwaldt, Alfons Baiker

Department of Chemistry and Applied Biosciences, Swiss Federal Institute of Technology, ETH Hönggerberg, 8093 Zürich, Switzerland



Supercritical CO_2 has been found to be an excellent reaction medium for a number of reactions that are conventionally gas-liquid reactions and can thus be transformed to one single phase. However the properties of the solvent can only be varied over a certain range. Therefore the addition of a co-solvent in small amounts may be beneficial leading to improved solubility and improved mass transport while preserving the environmental and technical benefits of $scCO_2$. In the selective oxidation of benzyl alcohol to benzaldehyde with oxygen over Pd/Al_2O_3, the addition of toluene in small amounts resulted in an increased TOF of 2500 h^{-1} *vs* 1500 h^{-1} obtained in neat CO_2. Phase behaviour and *in situ* IR studies were performed in order to gain more insight into the reaction. Also in the presence of toluene single phase conditions are essential for high catalytic activity. Interestingly, the pure alcohol and the toluene/alcohol 1/1 mixture performed similarly in the biphasic region, while in the single phase region the activity in the presence of toluene was higher. By ATR-IR it was shown that toluene is already at low pressure completely dissolved in the bulk supercritical phase, while an alcohol-rich liquid-like phase is present below 150 bar, as in the case of pure alcohol. This may imply that the presence of toluene does not have a strong impact on the phase behaviour but mainly improves the mass transfer or the surface properties of the catalyst.

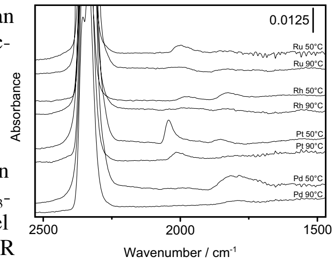
[1] M. Caravati, J.-D. Grunwaldt, A. Baiker, *Phys. Chem. Chem. Phys.* **2005**, *7,* 278.
[2] M. Caravati, J.-D. Grunwaldt, A. Baiker, *Submitted for publication*.

Physical Chemistry **333**

Supercritical CO_2 – An inert solvent for catalytic hydrogenation?

Marco Burgener, Davide Ferri, Jan-Dierk Grunwaldt, Tamas Mallat, and Alfons Baiker

Department of Chemistry and Applied Biosciences, Swiss Federal Institute of Technology, ETH Hönggerberg, CH-8093 Zurich, Switzerland



Supercritical carbon dioxide is an attractive solvent in hydrogenation reactions over solid catalysts. However, CO_2 may react on the surface of Pt-group metal particles with H_2 leading to poisonous CO. Therefore, surface species originating from the reaction between CO_2 and H_2 over Al_2O_3-supported Pt, Pd, Rh, and Ru model catalysts were investigated by ATR-IR spectroscopy under high pressure conditions. A batch reactor equipped with ATR-crystal and transmission IR windows and a continuous-flow cell with an internal reflection element were used. The study evidenced that CO formation from dense CO_2 in the presence of hydrogen is a feasible reaction over all Pt-group metals commonly used in heterogeneous catalytic hydrogenations in "supercritical" CO_2. In the batch reactor cell formation of CO was detected on all metals at 50 and 90°C, with the highest rate on Pt (see Fig.). Additional surface species were observed on Pt/Al_2O_3 at 150 bar under static conditions. In the continuous-flow cell, CO formation on Pt/Al_2O_3 was less extensive than in the batch reactor cell. From the studies we conclude that CO formation in CO_2-H_2 mixtures remains a minor side reaction during hydrogenation reactions on Pt-group metal catalysts and dense ("supercritical") CO_2 may be considered as an essentially inert solvent for practical applications. Still, in some cases even small amounts of CO adsorbed on specific surface sites can affect a structure sensitive hydrogenation reaction and may be the origin of unexpected shifts in the product distribution.

Physical Chemistry **335**

Vibrational relaxation and vibrational wavepackets in ultrafast time-resolved fluorescence measurements of perylene and derivatives

Anatolio Pigliucci, Guillaume Duvanel, Sébastien Cap and Eric Vauthey

Department of Physical Chemistry, University of Geneva,
30 quai Ernest Ansermet, CH-1211 Geneva, Switzerland

The initial step of most photoinduced processes in the condensed phase is vibrational relaxation (VR). Several photoinduced processes can occur on a timescale comparable to that of VR. However, the effect of VR on these processes has never been truly investigated because the parameters, which play a role during VR, are still largely unknown. In order to better understand VR and the role of the environment, ultrafast time-resolved fluorescence measurements have been carried out with Perylene and derivatives in different solvents. The use of ultrashort laser pulses to excite the molecule, leads to a superposition of vibrational states in the excited state. Therefore the early fluorescence dynamics does not only reveal VR but also exhibits the typical oscillation due to propagation of a vibrational wavepacket. A detailed study of both solvent and wavelength dependence of these processes will be presented.

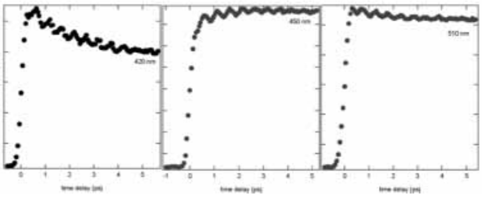


Figure: Early fluorescence dynamics of a Perylene at different wavelengths. Both VR and wavepackets propagation can be observed.

Physical Chemistry **334**

Reactivity of NO_3 on atmospheric mineral dust aerosol surrogates and laboratory flame soot

Federico Karagulian and Michel J. Rossi

Laboratoire de Pollution Atmosphérique et Sol (LPAS), Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne (Switzerland)

Atmospheric aerosol particles represent the single most uncertain factor in climate change owing to radiative forcing of greenhouse gases and troposheric aerosols. Deforestation and change of the land-use are among the main causes for mineral dust emission such as $CaCO_3$, natural limestone, Kaolinite, Saharan Dust and Arizona Test Dust. Combustion processes under fuel-rich conditions are the principal source for the emission of soot particles in the atmosphere. Both mineral dust and soot aerosols contribute to the reduction of atmospheric concentrations of trace gases like HNO_3, N_2O_5, O_3 and NO_3 with a strong consequence on the global ozone budget [1]. NO_3 represents a significant part of the oxidation potential of the atmosphere at night and has an important role as a free radical linking the nitrogen reservoirs HNO_3 and N_2O_5 to active nitrogen NO_y. Uptake experiments of NO_3 on mineral dust aerosols and soot particles were carried out under continuous molecular flow conditions at 298 ± 2 K using the thermal decomposition of N_2O_5 as a NO_3 source. In situ laser detection using Resonance Enhanced Multiphoton Ionization (REMPI) was used in addition to mass spectrometry in order to specifically detect NO_2 in the presence of N_2O_5 and NO_3. For mineral dust and soot particles we extrapolated an uptake coefficient $\gamma = 0.2 \pm 0.03$ for $[NO_3] \sim 1.0 \times 10^9$ molecule cm^{-3} close to tropospheric conditions. Adsorbed NO_3 gave rise to uptake of NO_2 γ of about 10^{-3}, whereas NO_2 by itself did not show any uptake on the analyzed substrates. The disappearance of NO_3 was accompanied by the formation of N_2O_5 or HNO_3 in variable proportions on mineral dust and by the formation of HONO on soot particles. Branching ratios of products will be presented as a function of experimental conditions.

Physical Chemistry **336**

Ultrafast Transient Grating Investigations at Liquid-Liquid Interfaces

Angela Punzi, Eric Vauthey

Dpt. of Physical Chemistry of the University of Geneva,
quai E.-Ansermet 30, 1211 Geneva 4, Switzerland

Liquid-liquid interfaces play an important role in many areas of sciences. However, because of the difficulty to probe selectively the interface, the dynamic of chemical processes at liquid-liquid interfaces is largely unknown.

We have undertaken some evanescent transient grating (TG) measurements [1] in order to be able to investigate ultrafast dynamics at interfaces. The intefacial selectivity is achieved by using an evanescent optical field generated upon total internal reflection (TIR) at the boundary region. Two types of measurements will be presented:

1) Population dynamics [2]: excited-state dynamics of the dye (Rhodamine 6G, R6G) at the methanol-decaline inteface has been compared to that of the bulk solution of the same dye. The observed shortening of the excited-state lifetime at the interface is ascribed to the adsorption and to the consequent strong self-quenching.

2) Energy hopping dynamics at the interface [2]: by using the cross grating (CG) technique, the anisotropy decay was observed to be much shorter of the diffusional reorientation time of the dye. This indicates that the main origin of the anisotropy decay is the energy hopping between R6G molecules, which occurs on an ultrafast time scale. The difference in energy hopping dynamics in bulk and at the interface will be discussed.

[1] P. Brodard, E. Vauthey, *J. Phys. Chem. B*, **2005**, 109, 4668.
[2] A. Punzi, P. Brodard, E. Vauthey, *Chimia* **2005**, *59*, 116.

Physical Chemistry **337**

Characterization of surface functional groups present on soot and on laboratory-generated secondary aerosols

Ari Setyan[a], Jean-Jacques Sauvain[a] and Michel J. Rossi[b]

[a]Institut Universitaire Romand de Santé au Travail, Rue du Bugnon 19, CH-1005 Lausanne, Switzerland
[b]Laboratoire de Pollution Atmosphérique et Sol (LPAS), Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland

A novel and promising method [1] has been used to characterize the surface functional groups present on soot and on laboratory-generated secondary aerosols. This method makes use of a heterogeneous chemical reaction between the aerosol condensed phase and a gas-phase probe molecule. For each type of functional group present on the aerosol surface (such as carbonyl, hydroxyl, acidic, basic and oxidizable groups, as well as adsorbed metal ions), the interaction of an appropriate titrant molecule specifically interacting with a single functional group is studied in a Knudsen flow reactor. The type and number of probe molecules taken up by a deposited aerosol sample, whose surface area has previously been measured, reveals the type and number of surface functional groups present on the aerosol surface. First results on a field measurement campaign, where the aerosols have been collected on high-volume sampler for subsequent interrogation by gas-phase probe molecules, will be reported.

[1] B. Demirdjian and M. J. Rossi, *Atmos. Chem. Phys. Discuss.* **2005**, *5*, 1-48.

Physical Chemistry **338**

A multidiagnostic stirred flow reactor for studying the kinetics and spectroscopy of ices

Simone Chiesa and Michel J. Rossi

Laboratoire de Pollution Atmosphérique et Sol (LPAS), Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland

A novel experimental apparatus is described and its potentialities discussed. By combining Fourier Transform Infra-Red (FTIR) Spectroscopy with a Quartz Crystal Microbalance (QCM) [1] it is possible to study the composition and structure of growing or evaporating thin ice films as a function of thickness (typically in the range from 100 nm to some microns). In a stainless steel reactor under vacuum, the use of the QCM gold-coated crystal as a temperature controlled deposition substrate allows very precise determination of mass changes. An IR beam is directed towards the ice film at a grazing incidence angle, of approximately 70°; under these conditions, the surface properties of the thin ice film sample are enhanced with respect to the bulk of the crystal. An IR polarizer can be used to study the very different interaction of S- and P-polarized light with the thin film and an understanding of its optical properties is therefore achievable. The experiments can be performed using both pure and doped ice: dopants employed are atmospherically relevant gases like HCl, HBr and HNO_3. This experiment has enabled a more complete investigation of the properties of one of the most important greenhouse gases in the atmosphere, namely condensed water vapour.

[1] C.Delval and M. J. Rossi, *Phys. Chem. Chem. Phys.,* **2004**, *6*, 4665.

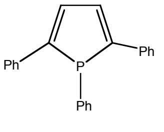
Physical Chemistry **339**

EPR and DFT studies of one-electron reduction of phospholes

Prashant Adkine,[a], Nicolas Mezailles,[b] Pascal Le Floch,* [b] Michel Geoffroy*[a]

[a] Department of Physical Chemistry, 30 Quai Ernest Ansermet, University of Geneva, 1211 Geneva 4 (Switzerland).
[b] Laboratoire Hétéroéléments et Coordination, UMR CNRS 7653, Département de Chimie, Ecole Polytechnique, 91128 Palaiseau Cedex (France).

The redox behaviours of 1,2,5 phenyl phosphol (**I**), 1- methyl 2,5 phenyl phosphol (**II**) and dibenzophosphol (**III**) have been studied by cyclic voltammetry. The structural modifications caused by one-electron reduction of these phospholes have been determined by DFT calculation. The EPR spectra recorded by electrochemical reduction *in situ* in the EPR cavity at low temperature, are compared with those, obtained by reaction with potassium, which were reported in early studies [1]. Information about spin delocalisation is obtained from both experimental and theoretical (DFT) hyperfine interaction.



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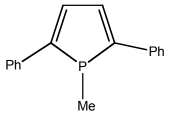

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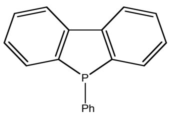


III

[1] D. Kilcast, C. Thomson, *Tetrahedron* **1971**, 27, 5705.

Physical Chemistry **340**

Oxidation Products of Bis-Iminophosphoranes: An EPR Study

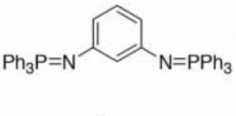
Adil Matni,[a] Leila Boubekeur,[b] Nicolas Mezailles,[b] P. Le Floch,* [b] Michel Geoffroy*[a]

[a] Department of Physical Chemistry, 30 Quai Ernest Ansermet, University of Geneva, 1211 Geneva 4 (Switzerland).
[b] Laboratoire Hétéroelements et Coordination, UMR CNRS 7653, Département de Chimie, Ecole Polytechnique, 91128 Palaiseau Cedex (France).

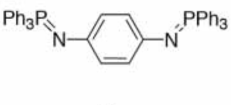
Chemical and electrochemical oxidations of the bis-iminophosphoranes B_{ortho}, B_{meta} and B_{para}, lead to the formation of radical cations, whose structures have been studied by EPR. The resulting hyperfine constants are compared with those predicted by DFT calculations.

Experimental and theorical results show that the unpaired electron is mainly delocalized on both the nitrogen atoms and the phenylene ring. The stability of the cation is slightly dependant upon the isomer.

$\mathbf{B_{ortho}}$



$\mathbf{B_{meta}}$



$\mathbf{B_{para}}$

Physical Chemistry **341**

Chiral gold nanoparticles

Cyrille Gautier and Thomas Bürgi

Université de Neuchâtel, Institut de Chimie, Av. de Bellevaux 51, 2007
Neuchâtel, Switzerland.

We have prepared small gold particles (< 2 nm) protected with a chiral thiol, N-acetyl-L-cysteine. These particles exhibited vibrational circular dichroism (VCD) activity in vibrations associated with the adsorbed N-acetyl-L-cysteine. Density functional theory (DFT) calculations of N-acetyl-L-cysteine adsorbed on gold clusters were used to simulate VCD spectra in order to determine the conformation of the adsorbed molecules. The calculated VCD spectrum of the most stable conformer of adsorbed N-acetyl-L-cysteine compared well with the experimental spectrum. The particles can be separated according to size and charge by gel electrophoresis. Such separations reveal high abundance of certain particle sizes (magic numbers). Furthermore, the separated fractions show electronic circular dichroism activity in transitions located in the metal core (Figure 1). Possible origins of this optical activity are discussed.

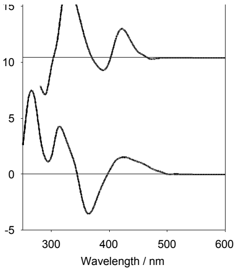


Figure 1: Circular dichroism (CD) spectra of N-acetyl-L-cysteine protected gold nanoparticles. The two spectra correspond to two different fractions separated by a gel electrophoresis of the raw material.

Physical Chemistry **342**

Probing enantiospecific interactions between proline and a chiral self-assembled monolayer by modulation excitation ATR-IR spectroscopy

Marco Bieri and Thomas Bürgi

Université de Neuchâtel, Institut de Chimie, Av. de Bellevaux 51, 2007
Neuchâtel, Switzerland.

The interaction of proline (selectand) with self-assembled monolayers (SAMs) of L-glutathione (*γ-glu-cys-gly*, selector) on gold was investigated by a combination of attenuated total reflection infrared (ATR-IR) and modulation excitation spectroscopy (MES).[1] The latter technique makes use of a phase-sensitive detection of periodically varying signals. By modulating the absolute configuration of the selectand (absolute configuration modulation) at the SAM interface, enantiospecific interactions can selectively and sensitively be spotted.[2], [3] By applying a convection-diffusion model coupled to adsorption and desorption it was possible to extract relative adsorption and desorption rates from the experimental data for the two enantiomers of proline, fully accounting for mass-transport within the ATR-IR flow-through cell. The results show that particularly the desorption kinetics is different for the two enantiomers. Therefore the L-glutathione SAM can discriminate between enantiomers, D-proline being stronger bound. The infrared spectra reveal that upon interaction with proline the adsorbed L-glutathione is protonated at the *gly* part of the molecule, which, in the absence of proline, is bound to the gold surface as carboxylate. The observed protonation of adsorbed L-glutathione upon interaction with proline goes along with a structural change of the former, which seems to play an important role for enantiodiscrimination.[4]

[1] D. Baurecht and U. P. Fringeli, *Rev. Sci. Instr.* **2001**, *72*, 3782.
[2] R. Wirz, T. Bürgi and A. Baiker, *Langmuir* **2003**, *19*, 785.
[3] R. Wirz, T. Bürgi, W. Lindner and A. Baiker, *Anal. Chem.*, **2004**, *76*, 5319.
[4] M. Bieri and T. Bürgi, *J. Phys. Chem. B* **2005**, *109*, 10243.

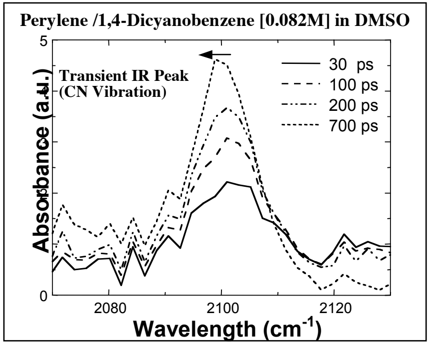
Physical Chemistry **343**

Structural Considerations in Photoinduced Bimolecular Electron Transfer – Time Dependent Visible and IR Transient Absorption

N. Banerji[1], B. Lang[1], O. Mohammed[2], E. Nibbering[2],
Th. Elsaesser[2], E. Vauthey[1*]

[1]University of Geneva, 30 Q. Ernest-Ansermet, 1211 Geneva 4, Switzerland
[2]Max-Born-Institut (MBI), Max-Born-Straße 2A, 12489 Berlin, Germany

Although bimolecular photoinduced electron transfer reactions have been intensively studied, there are many unanswered questions. One of them concerns the nature and structure of the primary ET quenching product (some kind of ion pair) and its conversion into free ions. The systems studied here have perylene as the chromophore and a quencher that is either a donor (dimethylaniline, 1,2,4-trimethoxybenzene) or an acceptor (1,2-dicyanoethylene, 1,4-dicyanobenzene, tetracyanoethylene). The dynamics are investigated by transient absorption in the visible as well as in the IR range (pumping the Pe → Pe* transition at 400nm, probing in the visible or IR region). In contrast to the transient spectrum in the visible, certain transient IR bands exhibit spectral differences between ion pairs and free ions. For example, the transient IR peak of the CN vibration for the Pe/1,4-DCB system in DMSO displays a shift of the maximum with a quencher concentration of 0.082M. Results obtained with systems having a different driving force for ET, in various solvents and with changing quencher concentration will also be presented.



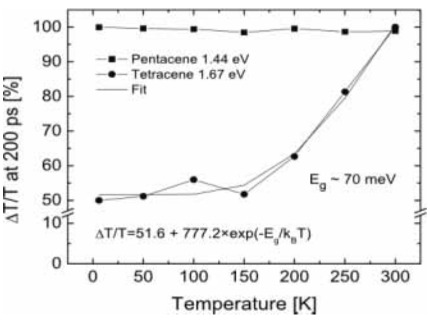
Physical Chemistry **344**

Temperature Dependence of the Ultrafast Dynamics in Pentacene versus Tetracene Crystals

Verner K. Thorsmølle, R. D. Averitt, J. Demsar, D. L. Smith, S. Tretiak,
R. L. Martin, X. Chi, A. P. Ramirez and A. J. Taylor

Los Alamos National Laboratory, Los Alamos, NM 87545.

Tetracene and pentacene belong to the polyacene series of organic crystals. In pentacene, the excitonic fission process from the lowest singlet exciton to a pair of lowest triplet excitons $S_1 \rightarrow 2T_1$ is energetically allowed, while in tetracene this same process is only possible by thermally activated fission [1,2].



Using ultrafast optical pump-probe spectroscopy we present the temperature dependence of the triplet production, branching ratios, and make a comparative study of the processes involved, which include singlet exciton recombination, singlet fission, and triplet state absorption.

[1] C. Jundt, G. Klein, B. Sipp, J. Le Moigne, M. Joucla and A. A. Villaeys, *Chem. Phys. Lett.*, **1995**, *241*, 84.
[2] S. V. Frolev, Ch. Kloc, J. H. Schön and B. Batlogg, *Chem. Phys. Lett.*, **2001**, *334*, 65.

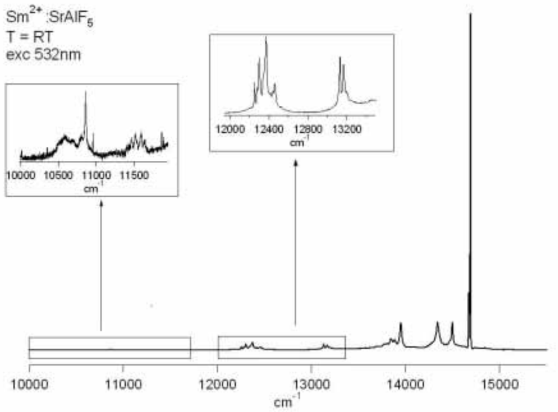
Physical Chemistry **345**

Luminescence of Sm^{2+} in $SrAlF_5$

T.Penhouet and H. Hagemann

Dépt. de Chimie Physique, Univ. de Genève, 30, q. E. Ansermet
1211 Genève 4

The crystal structure of $SrAlF_5$ presents 4 different Sr sites which can be substituted by Sm^{2+} [1]. Sm^{2+} has interesting properties for applications such as optical data storage by hole burning or as pressure sensor. Sm^{2+} can be used as a structural probe in a similar way as Eu^{3+}. The $^5D_0 - {}^7F_0$ transition of Sm^{2+} doped $SrAlF_5$ presents indeed 4 bands around 14670 cm^{-1} (two of which overlap), in agreement with the 4 available substituting sites. We have studied the intra-configurational emission of Sm^{2+} covering the entire range of $^5D_0 - {}^7F_J$ transitions (J = 0 to J = 6) using site-selective excitation and temperature-dependent measurements.



[1] F.Kubel, *Z. Anorg. Allg. Chem.* **1998**, *624*, 1481.

Physical Chemistry **346**

Visualisation of the electrode surface modified by polyelectrolytes and nanoparticles with scanning probe microscopy

C. Bradbury, J. Zhao, S. Huclova, E. Szöcs, H. Siegenthaler & D. J. Fermín

Department of Chemistry and Biochemistry, University of Bern
Freiestrasse 3, 3012, Bern, Switzerland

Considerable research is currently being conducted on the structure and properties of polyelectrolyte ultrathin films at surfaces. These films are constructed by electrostatic adsorption of polycations and polyanions on modified metal and metal oxide surfaces. The alternate deposition of polycations and polyanions is commonly referred to as the electrostratic layer-by-layer (LBL) assembly, pioneered by Decher[1]. Other charged species such as organic dyes, biomaterials and nanoparticles have been incorporated into such films for additional functionality. These LBL films have been used to control the properties of the surface in three dimensions at the nanometre scale. This process has found applications in hollow sphere capsules, separation membranes, chemical sensors and electro-optic devices.

Our group is particularly interested in the dynamics of electron transfer across these materials in the presence of metal and semiconductor nanoparticles[2]. In electrochemical systems, poly-electrolyte films can affect the rate of electron transfer by (i) increasing the distance between redox probes and the electrode surface (hinder electron transfer) or (ii) by changing the interfacial concentration of ionic active species (enhance or hinder electron transfer). The present contribution aims to gain further understanding on the structure of polyelectrolyte thin films by using Scanning Tunneling Microscopy (STM) and Atomic Force Microscopy (AFM). From the analysis of the surface structure, we expect to rationalise the electrochemical behaviour of these films in the presence and absence of metal nanoparticles.

[1] G. Decher, Science, **1997**, 277, 1232.
[2] J. J. Kakkassery, J-P. Abid, M. Carrara, & D. J. Fermín, Faraday Discuss., **2004**, 125, 157.

Physical Chemistry **347**

Intermolecular Electronic Communication between Molecules Assembled on Mesoscopic Oxide Films

Qing Wang, Shaik M. Zakeeruddin, and Michael Grätzel

Laboratory for Photonics and Interfaces, Ecole Polytechnique Fédérale,
CH-1015 Lausanne, Switzerland

Assembling organic or transition metal complexes on mesoscopic substrates has attracted much attention due to the potential applications in photovoltaics, electrochromism, light-emitting diode, etc. Understanding the electronic interaction between molecules is essential for the rational design and realization of devices with improved performances. Here we will show the intermolecular electronic communication and the consequent cross surface charge percolation of conjugated organic molecules or transition metal-complexes adsorbed on mesoscopic oxide films. The electrochemical and spectroscopic results will be discussed in this talk.

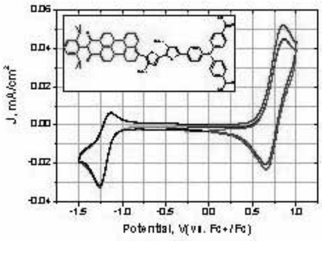


Figure 1. Cyclic voltammograms of inset molecule adsorbed on mesoscopic Al_2O_3 film in EMITFSI showing ambipolar charge percolations.

[1] P. Bonhote, E. Gogniat, S. Tingry, C. Barbe, N. Vlachopoulos, F. Lenzmann, P. Comte, M. Grätzel, *J. Phys. Chem. B* **1998**, *102*, 1498.
[2] Q. Wang, S. M. Zakeeruddin, J. Cremer, P. Bäuerle, R. Humphry-Baker, M. Grätzel, *J. Am. Chem. Soc.* **2005**, *127*, 5706.

Physical Chemistry **348**

Raman and ROA spectra of (3S)-2,2-diethyl-3-[(1E)-prop-1-enyl]cyclobutanone

Dmytro Dudenko, Werner Hug

Universität Freiburg, Chemin du Musée 9, CH-1700 Freiburg, Schweiz

An essential goal of the computation of Raman and Raman Optical Activity (ROA) spectra, and of our visualization of vibrational modes and the generation of Raman and ROA intensities in molecules [1], is finding links between molecular structure and observed spectra. The spectra of the title compound, which is of interest to the flavours and fragrances industry, have been computed with this goal in mind. They represent the superposition of the spectra of the four most stable conformers with a computed abundance of 39%, 17%, 11%, and 10%.

The geometry optimization and the force field were done at the DFT-B3LYP/6-311++G** level with Gaussian03, while the electronic tensors were obtained by a gauge-origin independent calculation with London orbitals at the TDHF/rDP level [2] with the Dalton program.

[1] W. Hug, Chem. Phys. **2001**, 264, 53.
[2] G. Zuber and W. Hug, J. Phys. Chem. A **2004**, 108, 2108-2118.

Physical Chemistry **349**

Spectroscopy of High Vibrational States of Water

Pavlo V. Maksyutenko [a], Oleg V. Boyarkin [a], John S. Muenter [b]
Thomas R. Rizzo [a]

[a] Laboratoire de Chimie Physique Moléculaire, Ecole Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland
[b] Department of Chemistry, University of Rochester, Rochester, New York 14627, USA

Water is the dominant absorber in the Earth's atmosphere, and knowledge of its high vibrational levels is important for determining weak absorptions in the visible and near-ultraviolet regions of the spectrum. *Ab initio* calculations of the energies and intensities of transition to these states need experimental values to test the validity of the potential energy and dipole moment surfaces at high energies. Experimental energies of the states with up to 8 quanta of OH stretch vibration (|0,8> in a local mode notation) have been previously determined. The aim of this work is to measure ro-vibrational levels in the region of |0,9> and |0,10>, providing a reference for the further improvement of water absorption calculations.

The absorption cross-sections for direct transitions to high overtone levels are extremely small, and the spectra are extremely congested. The use of double-resonance techniques has the advantage of providing more efficient access to these high levels while at the same time simplifies spectral congestions. Vibrational excitation with this method is performed in two steps: a first laser pulse promotes a water molecule a specific rotational state of |0,4>$^-$; a second laser pulse it is scanned over the transition from this intermediate state to |0,9> or |0,10>. The detection step consists in the selective dissociation of highly vibrationally excited molecules with a UV laser and subsequent laser-induced fluorescence of the OH fragments.

Our most recent results in the region of |0,9> and |0,10> will be presented.

Physical Chemistry **350**

Femtosecond Degenerate Four-Wave Mixing of Cyclopropane

Dominique S. Kummli, Hans M. Frey, Michael Keller und
Samuel Leutwyler

Departement für Chemie and Biochemie, Universität Bern, Schweiz

Femtosecond degenerate four-wave mixing (fs-DFWM) is applied to the measurement of rotational constants of cyclopropane (C_3H_6). The rotational coherence method yields a very accurate B_0 = 20 093.322(12) MHz and centrifugal distortion constants D_J and D_{JK} [1]. This accuracy is only surpassed by dipole distortion microwave spectroscopy. We have calculated the equilibrium structure, vibrationally averaged structure parameters and rotational constants with high-level *ab initio* methods using large basis sets. Combining these with the results of previous calculations and the measured rotational constants yields r_e(C-C) = 1.5034(3) Å , r_e(C-H) = 1.0775(5) Å and α_e(H-C-H) = 115.09(10)$^\infty$.

file=c3h6pub\s\do6(v)2.eps,angle=0, width=10.75cm

[1] Dominique S. Kummli, Hans M. Frey, Michael Keller and Samuel Leutwyler, *J. Chem. Phys.*, accepted, **2005**

Physical Chemistry **351**

Photochemistry and photophysics of light-controlled silver nanoparticle growth.

Andrea Callegari, Dino Tonti, Maurin Cornuz, Andrea Cannizzo, and Majed Chergui

Laboratoire de Spectroscopie Ultrarapide,
Ecole Polytechnique Fédérale de Lausanne, 1015 Lausanne

We have investigated the role played by photochemical and photophysical processes in the light-controlled formation of triangular silver nanoparticles from a colloidal solution of small spherical particles [1]. Using complementary spectroscopic techniques we have been able to distinguish the processes taking part in the growth, as well as several of the associated intermediate species. In particular, we have observed that light plays multiple roles: on one side, by driving a photochemical modification of the reagents, on the other side, in promoting the stepwise aggregation of the precursor nanoparticles.

[1] A. Callegari, D. Tonti, and M. Chergui, *Nano Letters* **3**, 1565 (2003).

Physical Chemistry **352**

Dynamics of Photoinduced Dye-to-Semiconductor Electron Transfer: Dependence upon the Density of Acceptor States

Bernard Wenger, Michael Grätzel and Jacques-E. Moser*

Laboratory for Photonics and Interfaces, Institute of Chemical Sciences and Engineering, Ecole Polytechnique Fédérale de Lausanne

Electron transfer (ET) from photoexcited Ru(II) polypyridyl complexes to nanocrystalline TiO_2 has been extensively studied due to its importance in the development of dye-sensitized solar cells [1]. The kinetics of charge injection was reported to be strongly multiexponential. Recently, we showed that this kinetic heterogeneity is mainly a consequence of a poor molecular ordering on the surface [2]. By carefully controlling the adsorption process, slow kinetic components could be turned off. The actual time constant for injection from $Ru^{II}(dcbpy)_2(NCS)_2$ sensitizer (N719) to TiO_2 was then found to be less than 20 fs.

ET kinetics are expected to depend directly upon the density of acceptor states (DOS). For charge injection dynamics, this parameter was experimentally investigated by use of various acceptors like ZnO, SnO_2 or Nb_2O_5 [1]. Unfortunately, measurements made with partially aggregated systems yielded multiexponential kinetics, whose dependence upon DOS could not be assigned clearly. In this contribution we report a time- and spectrally-resolved description of the excitation wavelength dependence of electron injection from N719 to nanocrystalline Nb_2O_5. Primary results show that two different mechanisms for dye deactivation exist, depending on the excitation wavelength. This observation suggests that observed kinetics indeed probed the DOS in the vicinity of the oxide conduction band edge. The mechanism will be discussed taking into account the spectral signature of the transient species.

[1] Anderson et al, *Coord. Chem. Rev.*, **2004**, *248*, 1231-1246.
[2] Wenger et al, *J. Am. Chem. Soc.*, **2005**, in press

Physical Chemistry **353**

Motional control of high Rydberg states of argon using time dependent electric fields

E .Vliegen, and F. Merkt*

Laboratorium für Physikalische Chemie ETH Zürich,
CH-8093 Zurich, Switzerland
vliegen@phys.chem.ethz.ch

We developed and tested a new technique using time dependent electric fields to decelerate argon in high-n Stark states and studied the implications for the deceleration of light molecules such as H_2.

When a particle, an atom or a molecule, is excited to a Stark state in an electric field F, the energy shift respective to the zero-field energy position is equal to $\Delta E = \frac{3}{2}nkF$, where k is used to label the Stark states and runs from $-(n - m_l - 1)$ to $(n - m_l - 1)$. By applying an inhomogeneous electric field, a force can be exerted on the particles and they can be decelerated or accelerated, depending on the sign of $k\nabla F$. In our previous setup the kinetic energy loss in the deceleration experiments was mainly limited by the life time of the Stark states which is approximately equal to $\tau = 10$ μs for an $n = 22$ Stark state. This caused the energy loss to be smaller than the Stark shift of the state excited and limited the maximal energy loss to be equal to $E_{\text{kin}}/hc = 10$ cm^{-1}, which is a factor of 6 smaller than the energy losses typically reached in experiments on polar molecules in their electronic ground state.

We show that with our new, more compact, setup: (1) the kinetic energy loss for a particle excited to a $n = 22$ Stark state is equal to the Stark shift when time independent fields are used; (2) the energy loss for any n can be larger than the Stark shift of the state that is excited when time dependent fields are used; (3) we can increase the maximal energy loss to $E_{\text{kin}}/hc \approx 60$ cm^{-1} All these results are compared with time-of-flight profiles calculated using trajectory calculations for particles in a Stark state. The electric fields in our setup were calculated using a commercially available finite element program [4]. We also discuss the possibility of decelerating H_2 with this setup using time dependent electric fields. Seeding H_2 in a rare gas will reduce the initial kinetic energy to well below 60 cm^{-1}.

Physical Chemistry **354**

Rotationally resolved PFI ZEKE photoelectron spectroscopy of ND$_3$

M. Raunhardt[1], M. Schäfer[1], F. Merkt[1], L. Duggan[2] and T. P. Softley[2]

[1]Laboratorium für Physikalische Chemie, Eidgenössische Technische Hochschule Zürich, ETH Hönggerberg, CH-8093 Zürich, Switzerland
[2]Department of Chemistry, Mansfield Road, Oxford OX1 3TA, UK

The pulsed-field-ionisation zero-kinetic-energy (PFI-ZEKE) photoelectron spectrum of ND_3 has been recorded in the vicinity of the first ionisation threshold following single-photon excitation from the ground state. The spectrum consists of rotationally resolved bands corresponding to transitions to the first three vibrational levels of ND_3^+ associated with the umbrella mode ($v_2^+ = 0, 1, 2$).

The rotational structure of bands with an odd v_2^+ value strongly differs from that of bands with an even v_2^+ value and are modelled theoretically using different approximations for the ionisation dynamics.

The spectra are compared with photoionisation spectra and their simulation by multichannel quantum defect theory (MQDT). The comparison with similar spectra recorded for NH_3 [1] reveals the importance of channel interactions in the photoionisation of ammonia and its isotopomers.

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Physical Chemistry **355**

HIGH-RESOLUTION PHOTOELECTRON SPECTROSCOPIC STUDY OF ALLENE

A. M. SCHULENBURG, S. WILLITSCH, F. MERKT*

Physical Chemistry, ETH Zürich, CH-8093 Zürich

The pulsed-field-ionisation zero-electron-kinetic-energy photoelectron spectrum of allene has been recorded in the region near the origin of the $\widetilde{X} - \widetilde{X}^+$ transition. The spectrum reveals a pronounced vibrational progression in the torsional mode ν_4 and several weaker vibrational bands. The rotational structure of these bands has been almost fully resolved and line positions as well as line intensities could be analysed in order to determine structural parameters of the $C_3H_4^+$ ion and to understand the photoionisation dynamics of allene. The rovibronic intensity distribution suggests a D_2 cationic structure with negligible torsional tunneling for the lowest two vibrational bands (v_4=0 and 1). The spectral intensities could be quantitatively reproduced using the recent model of Willitsch et al.[1] on the assumption that the electron is ionised out of a molecular orbital that can be represented by a linear combination of p_π and d_π components in a single centre expansion, whereby π refers to the projection of the orbital angualr momentum onto the main axis.

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Physical Chemistry **356**

High-Resolution Photoelectron Spectroscopy Study of the Energy Level Structure and Potential Curves of Xe_2^+

O. Zehnder, P. Rupper, F. Merkt*

Physical Chemistry, ETH Zürich (HCI), CH-8093 Zürich, Switzerland

The pulsed-field-ionization (PFI) zero-kinetic-energy (ZEKE) photoelectron spectrum of Xe_2 has been recorded between 90000 cm^{-1} and 108300 cm^{-1} following single-photon excitation with a broadly tunable VUV laser [1]. The spectrum consists of transitions from the ground neutral state X 0_g^+ of Xe_2 to the vibrational levels of the I(1/2u) state ($v^+ = 0 - 61$), the I(3/2g) state ($v^+ = 0 - 21$), the I(3/2u) state ($v^+ = 0 - 2$) and the II(1/2u) state ($v^+ = 0 - 11$). In addition the origin band of the Xe_2 X $0_g^+ \rightarrow Xe_2^+$ II(1/2g) transition has been observed. The experimental information has been used to derive potential curves for these states [2].

The potential model treats the three u and the three g curves globally and includes the effects of the long-range interactions as well as the spin-orbit interaction [3]. The potential parameters (six for the u states and six for the g states) have been determined in a least square fit to the observed levels. The potential curves are of spectroscopic accuracy (i.e. 1-5 cm^{-1}). These curves are compared with the most recent ab initio quantum chemical predictions [4].

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Physical Chemistry **357**

High-resolution measurements of the ns and nd Rydberg states of ortho H_2 and para D_2

H. A. Cruse, Th. A. Paul, E. Vliegen, H. J. Wörner and F. Merkt

Laboratorium für Physikalische Chemie, ETH Zürich, CH-8093 Zürich, Switzerland

New high-resolution measurements of transitions from the $B\,^1\Sigma_u^+$ state of ortho H_2 to high-n Rydberg states located below the $X\,^2\Sigma_g^+$ ($v^+ = 0,\ N^+ = 1$) threshold will be reported. Spectra were recorded by employing ultranarrow tunable laser sources in a double-resonance VUV-UV excitation sequence, $X\,^1\Sigma_g^+$ ($v'' = 0,\ J''$) $\rightarrow$ $B\,^1\Sigma_u^+$ ($v' = 2,\ J'$) $\rightarrow$ high n, $X\,^2\Sigma_g^+$ ($v^+ = 0,\ N^+$). VUV was generated by resonant four-wave mixing of the outputs of two pulsed Fourier-Transform-limited solid-state Ti:Sapphire laser systems. The spectral resolution of better than 200 MHz resulted in the partial resolution of the hyperfine structure. The evolution of the angular-momentum coupling with principal quantum number n will be discussed in the light of model MQDT calculations. From these measurements it was also possible to obtain new information on the decay dynamics of the high Rydberg states of H_2, and in particular to determine which high-n Rydberg states of H_2 are metastable and which decay by predissociation.

Similar measurements on para D_2 will also be presented. Millimetre wave measurements of the high-n Rydberg states of D_2 are planned, and the identification of the long-lived Rydberg states is a prerequisite for this work.

Physical Chemistry **358**

Millimetre Wave Spectroscopy and MQDT Calculations of High Rydberg States of Krypton: the Hyperfine Structure of $^{83}Kr^+$

Martin Schäfer, Frédéric Merkt[⋆]

ETH Zürich, Laboratorium für Physikalische Chemie,
ETH-Hönggerberg HCI, CH-8093 Zürich, Switzerland

A phase-stabilised backward wave oscillator (BWO) in the 260–380 GHz range was combined with a VUV laser system to record high-resolution spectra of high-n Rydberg states of krypton. Krypton atoms were excited into np (n=58,60) Rydberg states via the 4d[1/2] ($J = 1$) state using VUV and visible laser photons. Millimetre wave transitions between np and ns or nd Rydberg states were detected by pulsed field-ionisation, at sub-MHz resolution and with mass selection. Using this excitation scheme, very accurate relative energies of fine and hyperfine structure levels of ($n + 2$)s and nd (n=68–74) Rydberg states of ^{84}Kr and ^{83}Kr were obtained. In this region, s-d interactions are observable for ^{83}Kr due to the hyperfine interaction.

A multichannel quantum defect theory (MQDT) treatment of the hyperfine structure [1] was used to analyse the millimetre wave data in combination with recent high-resolution VUV laser data [1] and the available data from the literature; improved MQDT parameters and hyperfine structure data of the ^{2}P ground electronic state of ^{83}Kr$^+$ were obtained.

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Physical Chemistry **359**

Rotationally Resolved UV Spectra of Weakly Bound Complexes: Structures and Internal Motions

Martin Schäfer[⋆],
David R. Borst[†], Cheolhwa Kang[†], David W. Pratt[†]

[⋆]ETH Zürich, Laboratorium für Physikalische Chemie, ETH-Hönggerberg HCI, CH-8093 Zürich, Switzerland
[†]Department of Chemistry, University of Pittsburgh,
Pittsburgh, Pennsylvania 15260, USA

Rotationally resolved UV spectra of weakly bound complexes of aromatic molecules have been recorded using a frequency-doubled continuous-wave ring dye laser and a molecular beam apparatus. The measured rotational constants provide information about the structures of the complexes in their S_0 and S_1 states. Whereas N_2 has been found to be located above the aromatic ring plane in the complexes with aniline [1] and 1,4-difluorobenzene [2], *ortho*-H···O (or NC) and F···HO or CN···HO hydrogen bridges favour planar complexes between 1,4-difluorobenzene and water [3] or between benzonitrile and water [4], methanol or acetonitrile [5].

For all these complexes, the observed spectra consist of two subbands due to an internal motion. For some of these complexes, the values for the barriers hindering internal rotation change significantly upon excitation $S_1 \leftarrow S_0$.

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Physical Chemistry **360**

Analysis of the 6snp($J = 1$) Rydberg series of ytterbium

Urs Hollenstein[⋆], Sandro Hannemann[†], Eric-Jan van Duijn[†],
Hans Jakob Wörner[⋆], Wim Ubachs[†] and Frédéric Merkt[⋆]

[⋆]Laboratorium für Physikalische Chemie, ETH Hönggerberg,
CH-8093 Zürich, Switzerland

[†]Laser Centre, Department of Physics and Astronomy, Vrije Universiteit,
De Boelelaan 1081, 1081 HV Amsterdam, The Netherlands

High resolution spectra of the 6snp($J = 1$) $\leftarrow$ 6s^2 transitions in ytterbium are recorded in the range of 49 500 cm^{-1} to 50 360 cm^{-1} by laser induced fluorescence (LIF) detection. The spectra are measured using the frequency up-converted output of a tunable, narrow bandwidth Ti:sapphire (Ti:S) oscillator cavity (described in Ref. 1). With the resolution of 0.005 cm^{-1} it is possible to resolve the isotopic structure and the hyperfine structure of the transitions. The experimental spectra of the strongly perturbed Rydberg series are compared with a version of multi-channel quantum defect theory (MQDT) analysis, which includes the effect of nuclear spins [2,3] considering multiply excited perturbers, which belong to Rydberg series converging to higher ionisation thresholds [4,5].

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Physical Chemistry **361**

PFI-ZEKE spectroscopy of the cyclopentadienyl cation

H. J. Wörner and F. Merkt*

Physikalische Chemie, ETH Zürich, CH-8093 Zürich

This presentation summarizes the results of the first photoelectron spectroscopic study of the cyclopentadienyl cation. The cyclopentadienyl radical was produced in a supersonic expansion by photolysis of cyclopentadiene at 248 nm using the method described in Ref. [1]. PFI-ZEKE photoelectron spectra were recorded using two different excitation schemes. In the first experiment single-photon excitation from the $\tilde{X}$ $^2E''_1$ ground state of the radical was used to study the ground state of the cyclopentadienyl cation. In the second experiment, a resonance-enhanced two-photon excitation scheme via the vibrationless transition to the $\tilde{A}$ $^2A''_2$ state studied in Ref. [2] provided access to the first electronically excited state of the cyclopentadienyl cation. The analysis of the spectra reveals that the ground state of the cyclopentadienyl cation is a triplet state of electronic symmetry $^3A'_2$ and the first excited state is a singlet of symmetry $^1E'_2$, which is subject to a pronounced Jahn-Teller distortion. The results of *ab initio* calculations together with a preliminary analysis of the Jahn-Teller effect in the $^1E'_2$ state are presented.

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Physical Chemistry **362**

Femtosecond Degenerate Four-Wave Mixing of Carbondisulfide

Dominique S. Kummli, Hans M. Frey and Samuel Leutwyler

Departement für Chemie und Biochemie, Universität Bern, Schweiz

Femtosecond degenerate four-wave mixing (fs-DFWM) is applied for the measurement of rotational constants of carbondisulfide(CS_2). The rotational coherence method yields B_0, the centrifugal distortion constants D_J [1] of the $C^{34}S^{32}S$ and the $C^{32}S^{32}S$ isotopomers [1,2]. In addition we also can observe transitions due to the hotband of the bending vibration which is populated by 28 % at room temperature.

file=cs2.eps,angle=0, width=8.74cm

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Physical Chemistry **363**

CARBON NANOFIBERS GROWN ON METALLIC FILTERS AS NOVEL STRUCTURED CATALYTIC MATERIALS

P. Tribolet, L. Kiwi-Minsker

Ecole Polytechnique Fédérale, LGRC-ISIC-SB, CH-1015, Lausanne

The use of carbon nanofibers (CNF) as catalytic supports increases during the last decade. This is due to their high specific surface area without microporosity and graphitic structure, which improves conversion-selectivity pattern for some reactions. The majority of CNF catalysts have been used as fine powder. It makes them difficult to handle and induces high pressure drop in catalytic bed. To avoid this, CNF can be fixed to a support with desirable macrostructure, but it requires bindings and may affect the CNF properties. We report hereby novel catalytic materials consisting of CNF grown directly on sintered metal fiber (SMF) filters. The SMF consist of metal fibers with diameter of 8-40 μm and present advantages when used as supports due to high electro- and thermo-conductivity, open structure and filtration properties. The CNF on SMF filters were grown by catalytic decomposition of ethane in the presence of hydrogen at 630-705°C. The resulting composites consist of metallic fibers covered by a uniform thin layer (of few microns) CNF (Fig. 1) strongly encored to the metal surface. Pd°-nanoparticles were supported on CNF/$SMF_{Inconel}$ and the catalyst was tested in selective hydrogenation of acetylene showing improved performance.

Fig. 1: SEM pictures of CNF grown on SMF (Inconel) filter by catalytic decomposition of C_2H_6. Magnitude: A. 300x, B. 3000x, C. 20000x