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Organic Chemistry **333**

## Measurement of Orthogonal Dipolar C–F•••C=O Interactions

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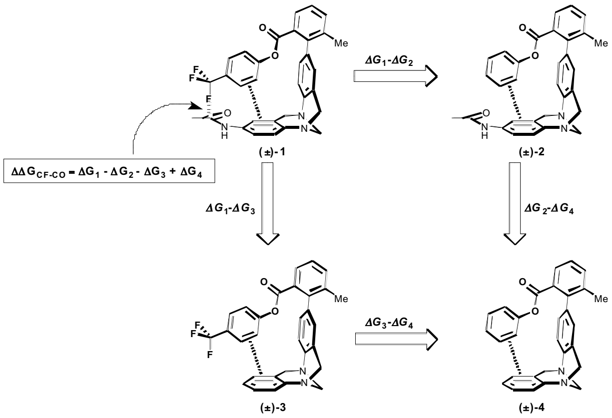
ETH Zürich, Hönggerberg, HCI, CH-8093 Zürich, Switzerland

In order to assess the free energy ΔG of an orthogonal C–F•••C=O dipolar interaction, we modified the *Wilcox* torsional balance. The molecule exists in two well-defined conformations. The equilibrium constant between a closed conformation where the $CF_3$ group of (±)**1** comes to rest within *Van der Waals* distance of the appended acetamide group on the face component and an open conformation is determined by NMR-spectroscopy. The perturbation of the major edge-to-face interaction is attributed to the dipolar interaction. Applying the double-mutant cycle provides accurate free energies for an orthogonal C–F•••C=O interaction [1].



[1] F. Hof, D. M. Scofield, W. B. Schweizer, F. Diederich, *Angew. Chem.* **2004**, *116*, 5166-5169; *Angew. Chem. Int. Ed.* **2004**, *43*, 5056-5059.

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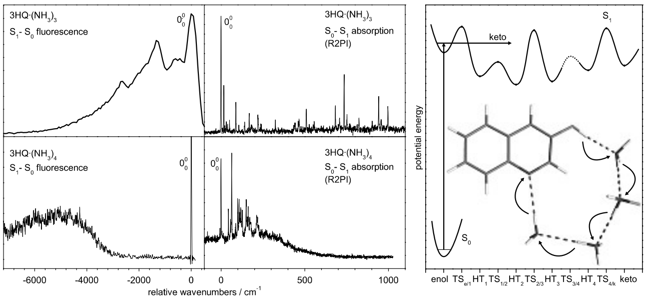
Physical Chemistry **334**

## Excited state H-atom translocation along a four-membered ammonia wire

Markus Thut, Andreas Steinlin and Samuel Leutwyler*

Universität Bern, Departement für Chemie und Biochemie,
Freiestrasse 3, 3012 Bern

We explore the entrance channel and reaction threshold of unidirectional excited state H-atom transfer reactions along hydrogen-bonded $(NH_3)_n$ wires and their dependence upon the number of constituents therein. $S_0 \rightarrow S_1$ excitation of supersonically cooled enol-3-hydroxyquinoline·$(NH_3)_4$ leads to H-atom transfer along the wire and emission from the keto- and/or intermediate species. On the other hand, the $n = 3$ cluster emits from the enol form without undergoing enol → keto reaction. *Ab initio* calculations predict translocation pathways from the $S_1$ enol-3HQ to its keto form, by passing several transition states and local minima. The number of constituents is crucial for the height of the first barrier and the profile of the $S_1$ potential energy hypersurface.



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Physical Chemistry **335**

## Conformation-specific ultraviolet and infrared spectroscopy of cold, protonated Ac-Phe-(Ala)$_5$-Lys and Phe-(Ala)$_{10}$-Lys: Spectroscopic signatures of gas phase helix formation

Jaime A. Stearns, Monia Guidi, Caroline Seaiby, Annette Svendsen, Oleg V. Boyarkin, and Thomas R. Rizzo

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

The alpha-helix is an important structural motif in biological molecules, and the factors governing its formation are being studied using a variety of techniques. One approach is to study helix-forming molecules in the gas phase to determine the characteristics intrinsic to the peptide which stabilize helical structures. Previous studies using ion mobility have suggested that polyalanines capped at the C-terminus with a lysine residue are helical in the gas phase, but are not helical in the absence of the lysine or with it at the N-terminus.[1] We have studied similar molecules with a phenylalanine chromophore using conformation-specific ultraviolet and infrared spectroscopy in a cold ion trap. We observe at least four conformers of Ac-Phe-(Ala)$_5$-Lys+H$^+$ but just a single major conformer of Phe-(Ala)$_{10}$-Lys+H$^+$. The amide N-H stretch frequencies provide signatures of the different types of hydrogen bonding present in each conformer. The bonding environments range from the free NH groups at the N-terminus of the peptides to amide groups in the center and C-terminus which are in strong helical N-H···O=C hydrogen bonds. The nonhelical molecules Ac-Lys-Phe-(Ala)$_{10}$+H$^+$ and Phe-(Ala)$_{10}$+H$^+$ provide a comparison by which we can determine the spectral signatures of helical molecules.

[1] M. Kohtani and M.F. Jarrold *J. Am. Chem. Soc.* **2004,** *126,* 8454.

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Physical Chemistry **336**

## Vibrational predissociation in hydrogen bonded dimer: The case of HF and its isotopomers

Carine Manca, Martin Quack, Martin Willeke

Physical chemistry, ETH Zurich, 8093 Zurich, Switzerland

We use $(HF)_2$ as a model system to understand the dynamics in hydrogen bonded systems. This particularly simple system has been widely used both in experimental and theoretical studies. Here we focus on the remarkable mode selectivity in vibrational predissociation process (VP) [1]. For instance, in experiments using highly resolved pulsed jet CW-CRDS, we have shown that the state involving two quanta of the bonded HF stretching mode has a VP lifetime $\tau_{PD}$ of only ~50 ps while that involving two quanta of the free HF stretching mode is more than 1 ns [2]. Measurements with the HF·DF isotopomer are currently in progress.

From a theoretical point of view, we have used the accurate fully 6-dimensional electronic potential hypersurface SO-3 established previously in our group [3] to study the VP with classical trajectory calculations. This combined study provides a more detailed understanding of the dynamics in this dimer. We present here our results of lifetimes and absorption spectra for several excitations involving the two stretching modes which we compare to the experimental results [4]. The theoretical work can also provide a benchmark in investigation for classical dynamics simulations.

[1] Note that the following references are non exhaustive but only exemplary: T. R. Dyke, B. J. Howard, W. J. Klemperer, *J. Chem. Phys.* **1972**, *56*, 2442; A. S. Pine, W. J. Lafferty, *J. Chem., Phys.* **1983**, *78*, 2154; K. von Puttkamer, M. Quack, *Mol. Phys.* **1987**, *62,* 1047; K. von Puttkamer, M. Quack, *Chem. Phys.* **1989**, *139*, 31; M. Quack, M. Suhm, *J. Chem. Phys.* **1991**, *95*, 28; M. von Dirke, Z. Bàcíc, D. H. Zhang, J. Z. H. Zhang, *J. Chem., Phys.* **1995**, *102*, 1382.

[2] M. Hippler, L. Oeltjen, M. Quack, *to be published.*

[3] W. Klopper, M. Quack, M. Suhm, *J. Chem. Phys.* **1998**, *108*, 10096.

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Organic Chemistry **333**

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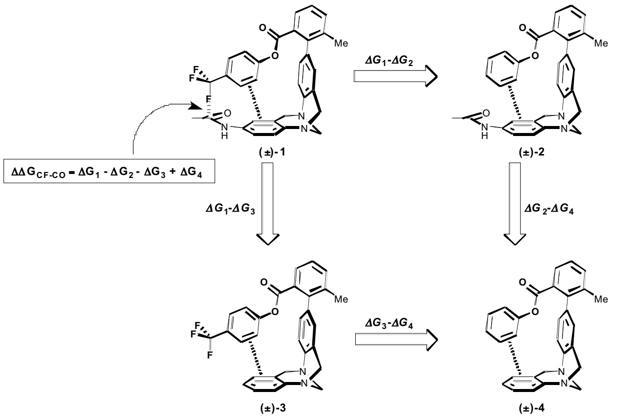

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Physical Chemistry **334**

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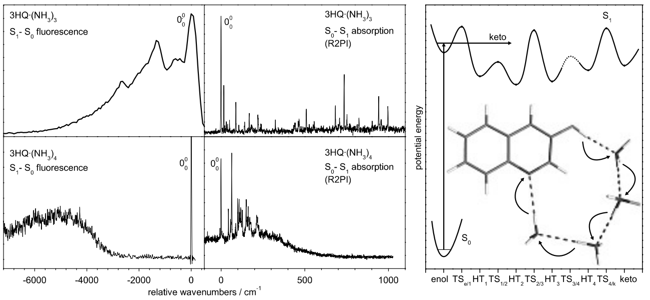

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Physical Chemistry **335**

## Conformation-specific ultraviolet and infrared spectroscopy of cold, protonated Ac-Phe-(Ala)$_5$-Lys and Phe-(Ala)$_{10}$-Lys: Spectroscopic signatures of gas phase helix formation

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

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Physical Chemistry **336**

## Vibrational predissociation in hydrogen bonded dimer: The case of HF and its isotopomers

Carine Manca, Martin Quack, Martin Willeke

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[4] C. Manca, M. Quack, M. Willeke, *in preparation.*

Physical Chemistry **337**

## A Zeeman decelerator for gas phase atoms and molecules

S. D. Hogan and F. Merkt

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With the goals of: (i) performing ultra-high resolution spectroscopy with long interaction times between a cloud of cold atoms or molecules and a narrow bandwidth radiation field, and (ii) studying cold reactive collisions in which the kinetic energies and quantum states of the colliding particles may be controlled to a high degree, a multi-stage Zeeman decelerator for neutral radicals has recently been developed in our laboratory [1]. This instrument relies on the same concept of phase stability employed in charged particle accelerators [2,3]. It opens up the possibility to manipulate the translational motion of a wider range of species than has been demonstrated using other quantum-state-selective techniques such as multi-stage Stark deceleration [4], and applies to a very different class of species than those to which Rydberg Stark deceleration is appropriate [5,6].

The results of a recent series of experiments in which we have decelerated ground state H and D atoms will be presented. In these experiments magnetic fields of 1-2 T were pulsed in each coil for tens of microseconds, with rise and fall times shorter than 5 $\mu$s. We have characterised the decelerated part of the gas pulse and studied the effect of zero field time windows, in which electron spin flips can occur, on the deceleration process. Approximately half of the kinetic energy of the atoms in a seeded supersonic expansion was removed with only 7 deceleration stages.

[1] N. Vanhaecke et al., *Phys. Rev. A*, **2007**, *75*, 031402.
[2] V. Veksler, *J. Phys. (USSR)*, **1945**, *9*, 153.
[3] E. M. McMillan, *Phys. Rev.*, **1945**, *68*, 143.
[4] H. L. Bethlem et al., *Phys. Rev. Lett.*, **1999**, *83*, 1558.
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[6] E. Vliegen and F. Merkt, *J. Phys. B*, **2006**, **39**, L241.

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Physical Chemistry **338**

## Structural Determination of a Short-lived Excited Iron (II) Complex by Ultrafast X-ray Absorption Spectroscopy

C.J. Milne,[1] W. Gawelda,[2] V.-T. Pham,[1] A. El Nahhas,[1] R. Vanderveen,[1] M. Benfatto,[3] Y. Zaushitsyn,[4] M. Kaiser,[5] A. Cannizzo,[1] D. Grolimund,[5] S.L. Johnson,[5] R. Abela,[5] A. Hauser,[6] C. Bressler,[1] and M. Chergui[1]

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[2]Instituto de Optica, CSIC, Calle Serrano 121, 28006 Madrid, Spain
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[6]Départment de Chimie Physique, Université de Genève, CH-1121 Genève, Switzerland

Structural changes of the aqueous $[Fe^{II}(bpy)_3]^{2+}$ complex induced by ultrashort laser pulse excitation at 400 nm and population of its shortlived quintet high-spin state have been detected by a combination of femtosecond fluorescence up-conversion and transient absorption spectroscopies [1,2], as well as picosecond x-ray absorption spectroscopy (XAS)[3]. The optical results indicate an ultrafast energy transfer from the excited $^1$MLCT state to the $^3$MLCT state (<20 fs) followed by relaxation through to the quintet state in less then a ps. Complete relaxation back to the singlet ground state occurs in $\leq$0.65 ns. A combined analysis of the XANES and EXAFS features measured 50 ps after excitation at the MicroXAS beamline at the Swiss Light Source indicates an Fe–N bond elongation of 0.2Å in the quintet state compared to the singlet ground state. The advent of novel femtosecond x-ray sources [4] should allow measurement of the change in charge density surrounding the Fe atom during the initial energy transfer steps giving previously inaccessible information about the spin-crossover process from the singlet to quintet states.

[1] W. Gawelda et al., CHIMIA, **2007**, in press.
[2] W. Gawelda et al., *J. Am. Chem. Soc.*, **2007**, submitted.
[3] W. Gawelda et al., *Phys. Rev. Lett.*, **2007**, *Vol.* 98, 057401.
[4] http://femto.web.psi.ch/

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Physical Chemistry **339**

## State-Resolved Studies of Silane Chemisorption on Si(100)

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Laboratoire Chimie Physique Moléculaire,
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CH-1015 Lausanne

We present recent data on the state-resolved reactivity of silane ($SiH_4$) on the Si(100)-(2x1) surface. Our results demonstrate a co-existence of both direct and precursor mediated mechanisms for the dissociative chemisorption of $SiH_4$ on Si(100) at surface temperatures of 373K and 473K. In the direct pathway, we find that the reactivity of $SiH_4$ is enhanced by both translational and vibrational energy of the incident molecules. In the precursor pathway, however, vibrational energy increases the reactivity, while translational energy decreases the reactivity of $SiH_4$. Vibrationally enhanced reactivity of a precursor mediated gas-surface reaction is observed here for the first time which gives information about the lifetime of vibrationally excited $SiH_4$ on Si(100). We also present evidence for mode-specific reactivity of $SiH_4$ on Si(100) by comparing state resolved sticking coefficients of $SiH_4$ for two nearly iso-energetic vibrational states $v_1+v_3$ and $2v_3$. These results demonstrate that the mode-specific reactivity of methane on Ni(100) observed by us previously is not an isolated case, a fact which emphasizes the importance of multi-dimension calculation of gas-surface reaction dynamics.

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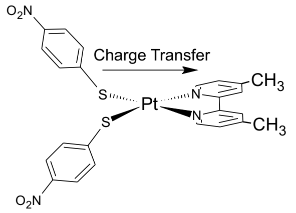
Physical Chemistry **340**

## Structural Reorganization in Photoexcited Organometallic Complexes Studied by Picosecond X-Ray Absorption Spectroscopy

R. M. van der Veen*†, V.-T. Pham*, A. ElNahhas*, C. J. Milne*†, C. Borca†, R. Abela†, J. Best‡, J. A. Weinstein‡, C. Bressler*, M. Chergui*

*École Polytechnique Fédérale de Lausanne, Laboratory of Ultrafast Spectroscopy, Lausanne, Switzerland
†Paul Scherrer Institut, Swiss Light Source, Villigen, Switzerland
‡The University of Sheffield, Sheffield, United Kingdom

Photoactive coordinatively unsaturated metal complexes are attractive chromophores for light-energy conversion, photocatalysis and chemical sensing in biological systems such as DNA. An important prerequisite for these applications is the existence of a long-lived charge-separated excited state. Square-planar Pt(II) diimine bis(thiolate) complexes are a promising class of these molecules, as their lowest excited state is of mixed thiolate/Pt-to-diimine charge transfer character and there is the possibility of structural reorganization in the excited state involving the formation of a three-electron sulfur-sulfur bond. This structural reorganization would act as an energy barrier preventing facile back-transfer and is thus a powerful tool to both prolong and tune the excited state lifetime of these complexes. By using ultrafast x-ray absorption spectroscopy, we aim to show the existence of the transient sulfur-sulfur bond and to determine its influence on the excited state properties.



Physical Chemistry **341**

### Conformationally dependent Rebinding Molecular Dynamics Simulations of Nitric Oxide to the V68FMyoglobin Mutant

Stefka Tsintsarska, Markus Meuwly

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

The study and modelling of reactive processes in chemically and biologically relevant systems has been always an interesting scientific topic. Here, an atomistically detailed picture of NO rebinding from myoglobin V68F is presented. Using reactive molecular dynamics [1] the rebinding probability as a function of time after dissociation is calculated. Reactive molecular dynamics considers two intersecting potential energy manifolds which dissociate to different adiabatic states. During the simulations, crossings are detected by monitoring an energy criterion and the surfaces are mixed over a finite number of time steps. The unbound surface (Fe...NO) is a standard force field, whereas the bound surface (Fe-NO) is based on ab initio calculations. The rebinding is nonexponential in time, in agreement with experimental studies [2] and can be described using two time constants. Particular emphasis is paid to the asymptotic separation Δ between the two potential energy manifolds. An extension of the original reactive molecular dynamics approach with a conformationally varying Δ is discussed and implemented. The advantages and the results of the conformationally dependant and conformationally independent Δ - function implementations are analized and compared.

[1] D.R. Nutt and M. Meuwly, *Biophys. J.* **2006**, *90*, 1191.
[2] Y. Wang, J.S. Baskin, T. Xia and A.H. Zewail, *Proc. Nat. Acad. Sci. USA* **2004**, *101*, *52,* 18000.

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Physical Chemistry **343**

### Electron energy distributions in associative detachment reactions of $O^-$ with $H_2$ and NO

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1700 Fribourg, Switzerland

We have measured electron energy distributions of the electrons detached in low-energy collisions

$$O^- + H_2 \rightarrow H_2O + e \qquad (1)$$

$$O^- + NO \rightarrow NO_2 + e \qquad (2).$$

The reactant $O^-$ ions have been created via dissociative electron attachment to $N_2O$ in the vicinity of a heated filament, focused by an ion lens system and crossed at 90° with the neutral $H_2$ or NO beam. The electron kinetic energy distributions have been measured using a magnetically collimated electron spectrometer.

A distinctly different behavior has been found for reactions (1) and (2). In the first case, the electrons carry away only minor amount of the available energy and the product $H_2O$ molecule is left in highly excited vibrational states. In the $O^-$/ NO collisions, the electron energies extend up to the allowed limit given by the reaction exothermicity. The observed behavior is explained on the basis of the widths of the involved resonances. In addition, we observed weak structures in the electron energy spectra, which we correlate with the vibrational levels of product molecules. Finally, absence of the electron signal in the $O^- + O_2$ collisions is discussed.

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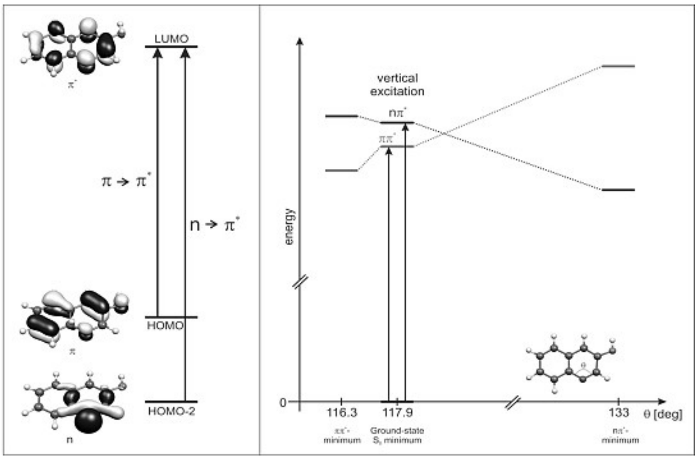
Physical Chemistry **342**

### ππ* vs. nπ* state photoreactivity of hydroxyquinolines

Andreas Steinlin, Markus Thut, Carmen Blum, Cornelia Heid,
Samuel Leutwyler

Departement für Chemie und Biochemie, Freiestrasse 3, Universität Bern,
3012 Bern, Switzerland

The $S_0 \rightarrow S_1$ electronic transitions of 3-, 6- and 7-hydroxyquinoline are ππ* (HOMO→LUMO) excitations, while the $S_0 \rightarrow S_2$ transitions are nπ* (HOMO-2→ LUMO). These three hydroxyquinolines are important chromophores in which to study excited state proton and/ or H-atom relays, i.e., $H^+$ or H transfer along hydrogen-bonded solvent wires. We have identified two intramolecular coordinates that lead to inversion of the ππ* and nπ* states. Excitation of the corresponding intramolecular $S_0 \rightarrow S_1$ vibronic transitions promotes the state inversion followed by nonradiative processes.



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Physical Chemistry **344**

### A study of the photoionization of $SiH_4$ near its adiabatic ionization threshold

M. Grütter, F. Merkt*

Laboratorium für Physikalische Chemie, ETH Zurich, 8093 Zurich,
Switzerland

The silane cation is subject to a Jahn-Teller distortion and *ab initio* calculations [1] show a $C_s$ minimum geometry in $SiH_4^+$. The equilibrium geometry can be described as an almost free-rotating $H_2$ unit weakly coupled to a $SiH_2^+$ cation.

Photoionization and threshold photoelectron spectra of $SiH_4$ have been studied near the adiabatic ionization threshold all the way up to the $SiH_2^+ + H_2$ dissociative ionization threshold. The pulsed-field-ionization zero-kinetic-energy (PFI-ZEKE) photoelectron spectra of $SiH_4$ near the dissociative ionization threshold ($\approx$ 92970 $cm^{-1}$) appear structureless which indicates a high density of states in the cation and is compatible with a large amplitude motion in the cation.

Literature values for the adiabatic ionization threshold of $SiH_4$ differ widely, from 11.0 eV in Ref. [2] to 11.6 eV in Ref. [3]. The experimental estimation of the dissociative ionization threshold to $SiH_2^+ + H_2$ enables us to confirm the result of Berkowitz *et al.* PFI-ZEKE photoelectron spectroscopy in the vicinity of the adiabatic ionization threshold will also be presented.

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Physical Chemistry **345**

## Conductivity measurements of a redox-active ionic liquid using terahertz time-domain spectroscopy

Verner K. Thorsmølle, Daibin Kuang, Shaik M. Zakeeruddin,
Guido Rothenberger, Michael Grätzel, and Jacques-E. Moser *

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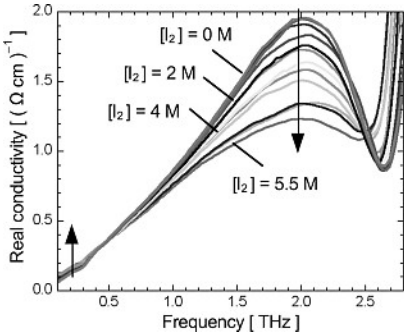
Ionic liquids have recently attracted much attention due to their unique properties, which include high electric conductivity and non-volatility, making them versatile alternatives to conventional applications, such as in dye-sensitized solar cells. Here we investigate the properties of the ionic and electronic conductivity pathways, including Grotthuse charge transfer [1], in 1-propyl-3-methyl-imidazolium iodide (PMII), using terahertz time-domain spectroscopy (THz-TDS), as a function of the molar concentration of iodine dopant and temperature.



*Real conductivity versus frequency at increasing molar concentrations of $I_2$ dissolved in PMII ionic liquid*

[1] R. Kawano and M. Watanabe, *Chem. Commun.* **2003**, 330-331.

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Physical Chemistry **346**

## Analysis of Structures and IR Spectra of Mixed Ices by MD Simulations

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Infrared spectra of mixed ices are important for the analysis of interstellar and cirumstellar grain mantles and for ice structures in star formation regions. For this purpose, numerous infrared (IR) experiments have been performed on these systems in the past.[1]

To understand the relation between characteristic infrared absorption bands and the corresponding structures, molecular dynamics (MD) simulations have been carried out on water ice systems combined with different trace molecules such as CO, $CO_2$, acetone and methane.

The IR spectra of these systems have been evaluated and related to structural features of the corresponding ice. To compare the IR spectra to experiment, accurate atomistic force field potentials have been used, which include anharmonic potentials for the bond terms and distributed multipole potentials[2] for the electrostatics.

[1] P. Gerakines, W. Schutte, J. Greenberg and E. v. Dishoeck, *Astron. Astrophys.*, **1995**, 296, 810-818
[2] A.J. Stone, *J.Chem.Theory Comput.*, **2005,** 1 , 1128.

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Physical Chemistry **347**

## Catalytic aerobic alcohol oxidation on mixed oxide supported Au nanoparticles – an *in situ* IR and XAS study

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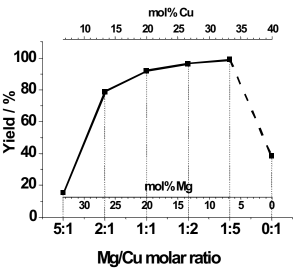
Gold-based catalysts have been successfully employed for several reactions [1]. In the present contribution, gold nanoparticles were deposited on mixed oxides containing Cu, Mg and Al in different ratios [2]. The mixed oxide-supported Au catalysts were investigated concerning their structural properties and tested in the aerobic liquid phase oxidation of 1-phenylethanol to phenyl methyl ketone affording TOFs up to 1300 $h^{-1}$ at excellent selectivity (>98%). The activity of these catalysts is strongly affected by the molar Mg/Cu ratio of the mixed oxide support (Fig. 1).



$CO_2$ adsorption from the liquid phase combined with in situ ATR-IR and modulation excitation spectroscopy indicated differences in the basic surface properties of the mixed oxides. Monodentate and bidentate carbonates were identified, the former being dominant on ternary Cu-containing supports. Liquid phase *in situ* XANES experiments showed the oxidation state of various supported Au catalysts. The results suggest that $Au^0$ is the active species in catalytic aerobic alcohol oxidation.

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[2] P. Haider, A. Baiker, *J. Catal.* **2007**, in press

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Physical Chemistry **348**

## A novel polychromatic femtosecond time-resolved fluorescence set-up in the UV for investigation of biological and chemical systems

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Time-resolved luminescence spectroscopy is beyond all doubts a powerful tool to investigate dynamical behavior of many physical systems and reaction pathways, in particular in the condensed phase. Fluorescence up conversion set-ups, based on the non linear phenomenon of sum frequency generation,[1] permits detection of time-resolved emissions with femtosecond resolution. With this technique we are then able to study ultrafast dynamics of different molecular systems, in particular proteins, and different phenomena such as solvation relaxation and cooling processes. In this respect, the present work is framed in a wider one aimed to probe the earliest dynamics of a wide variety of wild-type proteins, by means of ultrafast broad-band emission detection of optically active amino acids, as tryptophan, tyrosine and phenylalanine,[2] which all absorb in the UV range. Though up-conversion-based set-ups have been successfully implemented in the visible range, both for single wavelength and broad-band detection, only monochromatic detection measurements have been carried out in the UV. Here, we present for the first time a broad-band ultrafast fluorescence up-conversion set-up in this spectral range, with a detection range of 300-550 nm, a state-of-the-art time resolution of 330 fs, and a tunable excitation from 250 to 300 nm. We will present results on time-resolved fluorescence emission of some UV dyes in order to show the capability of the technique to study solvation dynamics. As a first application we report a preliminary investigation of tryptophan in water.

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[2] S. Schenkl et al., *Science*, **2005**, 309, 917.

Physical Chemistry **349**

### High resolution infrared spectroscopy of cyanodiacetylene ($HC_5N$): Rovibrational analysis between 900 and 4000 $cm^{-1}$ of its fundamental bands $\nu_1$,$\nu_3$, $2\nu_5$, $2\nu_7$ and $\nu_3 + \nu_5$ and associated hot bands

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New detection schemes in interstellar and planetary spectroscopy like the Infrared Space Observatory (ISO) make it now possible to identify and confirm the existence of linear carbon chain molecules, polyynes and cyanopolyynes, in the interstellar medium (ISM) [1]. These classes of molecules are of a particular interest with respect of the origin of life [2]. In 1976, Avery et al. [3] reported the first interstellar detection of the cyanodiacetylene, $HC_5N$, in the molecular cloud Sgr B2 by microwave spectroscopy after the first detection of its laboratory microwave spectrum [4]. For these reasons, we have studied this molecule in the mid-infrared region (900 – 4000 $cm^{-1}$). The molecule is also of interest in connection of intramolecular vibrational redistribution (IVR) of the acetylenic CH-stretching chromophore [5].

We have recorded the room temperature infrared spectrum of $HC_5N$ with our Zürich Bruker 2001 prototype Fourier transform infrared spectrometer [6] with a Doppler width ranged from 0.0009 to 0.0024 $cm^{-1}$ and a resolution from 0.0010 to 0.0017 $cm^{-1}$. The assignment and analysis were based on a detailed analysis of its submillimeter spectrum [3,7,8] and theoretical work [9]. We will discuss the analysis of the fundamental bands of the five vibrational states $\nu_1$ = 3330.14976 $cm^{-1}$, $\nu_3$ = 2190.954898 $cm^{-1}$, $2\nu_5$ = 2335.277969 $cm^{-1}$, $2\nu_7$ = 1271.966023 $cm^{-1}$ and $\nu_3 + \nu_5$ = 3315.824395 $cm^{-1}$, and their associated hot bands [10].

[1] P. Thaddeus and M.C. McCarthy, *Spectrochim. Acta A* **2001**, *57*, 757.
[2] L.E. Orgel, *Origins of Life* **2002**, *32*, 279.
[3] L.W. Avery et al., *Astrophys. J.* **1976**, *205*, L73.
[4] A.J. Alexander, et al., *J. Mol. Spectrosc.* **1976**, *62*, 175.
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[6] S. Albert, et al., *Trends. in Optics and Photonics* **2003**, *84*, 177. [7] K.M.T. Yamada and G. Winnewisser, *Z. Naturforsch. A: Phys. Phys. Chem. Kosmophys.* **1981**, *36A*, 1052.
[8] S. Haas, G. Winnewisser and K.M.T. Yamada, *Can. J. Phys.* **1994**, *72*, 1165.
[9] P. Botschwina, et al., *Spectrochim. Acta A* **1997**, *53*, 1079.
[10] Z. Guennoun, S. Albert and M. Quack, to be published.

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Physical Chemistry **351**

### Studies of molecular properties and slow exchange using Singlet-State Spectroscopy

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and Geoffrey Bodenhausen[1]

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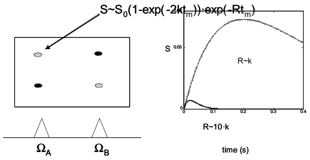
Singlet states, on which the normally dominant relaxation mechanism of dipole-dipole interaction between the involved spins is inoperative, are characterized by lifetimes that may have relaxation rates of up to 37 times slower than the longitudinal relaxation rate (observed in a sugar molecule). Using these slow relaxation rates, two-dimensional singlet-state exchange spectroscopy, SS-EXSY (1), can follow slow exchange rates between two states (A and B) in a 2D experiment (figure). This has been demonstrated for the ring protons of Tyr in the protein BPTI.



The relaxation rates of singlet states are determined by the chemical shift anisotropy and by dipole-dipole interactions to remote spins. The interpretation of the experimentally determined singlet-state relaxation rates in terms of CSA tensors and DD interactions provides insight into molecular symmetry, structure, and dynamics.

(1) R. Sarkar, P. R. Vasos and G. Bodenhausen, J. Am. Chem. Soc., 129, (2007), 328-334

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Physical Chemistry **350**

### Structural Analysis of Cu(II) Ligation to the GMP Nucleotide by Using Pulse EPR Spectroscopy

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Z-DNA is a higher energetic form of DNA. In contrast to the normal prevailing right-handed form of DNA (B-DNA), Z-DNA displays a left-handed helix.[1] Substochiometric amounts of propylene bridged bis-(di-((3',5'-dimethyl-pyrazoyl)-2-ethyl)-amine) dicopper complex were able to convert poly d(CG) from the right- to the left-handed conformation. The action of the copper as well as nickel dinuclear complexes can easily be reversed by addition of EDTA.[2]

In this work, we used the CuGMP (GMP: 5'-guanosine monophosphate) as a model system to understand the role of the metal-(poly)nucleotide interaction. The basic aim of the present work is to carry out, by Pulse EPR spectroscopy, a detailed analysis of the electronic and geometric structures of the CuGMP complexes with different isotopically labeled GMP ligands. Continuous-wave and pulse EPR methods like ENDOR and HYSCORE provide unique information about the electronic and geometric structure of these copper compounds through an elaborate mapping of the hyperfine and nuclear quadrupole interactions between the unpaired electron of the Cu(II) ion and the magnetic nuclei of the nucleotide ligand.[3] In addition, we have begun to study the interaction of copper with poly d(GC).

[†] deceased on 4 January 2006

[1] B. Spingler, F. Zobi, P. M. Antoni, A. Medina-Molner, R. Alberto, *Chimia* **2005**, *59*, 826-831.
[2] P. M. Antoni, B. Spingler, *Chem. Eur. J.* **2007**, in press.
[3] M. G. Santangelo, A. Medina-Molner, A. Schweiger, G. Mitrikas, B. Spingler, *J. Biol. Inorg. Chem.* **2007**, in press.

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Physical Chemistry **352**

### ELECRON-DRIVEN CHEMISTRY TO ETHERS

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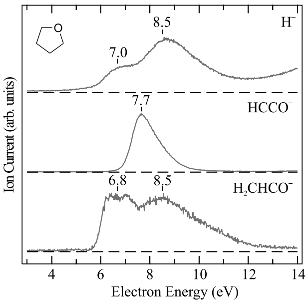
The interest in chemical processes induced by electrons increased in the last years due to new discoveries in radiation damage of the DNA [1] and due to new and modern applications in material science.

In earlier works we studied compounds containing hydroxyl and amino groups which can be considered to be models for biomolecules [2]. We extend our work to the study of the fragmentation of the ether bond, found in ribose and tetrahydrofuran (THF).



The high energy bands are assigned to Feshbach resonances while the additional bands at lower energies observed in some linear ethers are due to shape resonances. The calculated thresholds for DEA to ethers suggest that the low energy processes are proceeding with an activation barrier.

P.D.Burrow *et co.* have shown that the DEA cross section of THF is much smaller than that of the alcohols [3]. Our observation from diethylether suggests that the C-O bond in THF also fragments efficiently, but the resulting ion is metastable and its lifetime is too short to be detected.

[1] B. Boudaiffa, P. Cloutier, D. Hunting, M.A.Huels, L. Sanche, *Science*, **2000**, 287, 1658.
[2] T. Skalicky and M. Allan, *J. Phys. B*, **2004**, 37, 4849
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Physical Chemistry **353**

## Chiroptical properties of chiral gold nanoparticles

Cyrille Gautier, Thomas Bürgi*

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Monolayer protected nanoparticles are fascinating hybrid materials. Their physical and chemical properties can easily be tuned for custom requirement. Their potential applications were reported in various fields such as catalysis, sensing, therapy, electronics and optics. The subnanometer class of gold nanoparticles covered with chiral thiols shows optical activities both in the UV-vis and in the IR. This optical activity has important implications in fundamental research. The comparison of calculated and experimental vibrational circular dichroism spectra has been used successfully to determine the conformations of N-acetyl-cysteine and N-isobutyryl-cysteine (NIC) absorbed on small gold nanoparticles.[1,2] The calculated conformations were in good agreement with those reported for a self-assembled-monolayer on extended gold surfaces.[3] The nanoparticles protected with NIC and 1,1'-binaphtyl-2,2'dithiol were separated according to their size by electrophoresis and size exclusion chromatography, respectively.[2] Whereas the optical activity in the IR remained unchanged, the optical activity in the UV-vis was strongly size dependent. These results clearly demonstrate the power of chiroptical techniques to selectively probe the conformation of chiral adsorbates in the IR region and the structure of the metallic part in the UV-vis. Meanwhile, the origin of the optical activity located in metal based transitions and whether the metal core is intrinsically chiral remain open questions due to the lack of direct structural information.

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[2] Gautier C, Bürgi T, *J. Am. Chem. Soc.* **2006**, 128, *11079*
[3] Bieri M, Bürgi T, *J. Phys. Chem. B* **2005**, 109, *22476*

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Physical Chemistry **354**

## Dynamics of Ultrafast Light-Induced Electron Transfer through *p*-Phenylene Spacer Bridges under Non-Equilibrium Conditions

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Photochemical Dynamics Group [1] and Laboratory for Photonics & Interfaces,[2] Ecole Polytechnique Fédérale de Lausanne,
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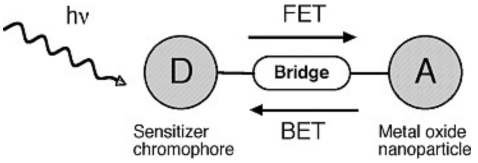
The effect of electronic and nuclear factors on the dynamics of dye-to-semiconductor photo-induced electron transfer was studied employing $Ru^{II}$(terpy)$(NCS)_3$ dye-sensitizer complexes grafted onto transparent films made of titanium dioxide nanoparticles. Phosphonic groups allowed for the anchoring of the dyes onto $TiO_2$ nanocrystalline films. The kinetics of interfacial charge transfer was recorded by use of time-resolved spectroscopy in the fs-ps domain.



The presence of oligo-*p*-phenylene spacer bridges of increasing length influenced the dynamics of both forward light-induced electron transfer (FET) and thermal back transfer (BET), although with a much weaker effect in the case of FET ($\beta = 0.19$ Å$^{-1}$ and 0.50 Å$^{-1}$ for FET and BET, respectively).

The weak distance dependence of FET strongly suggests a non-equilibrium vibrationally-assisted electron transfer process was effective. Experimental results can be rationalized by considering that tunneling electrons were coupled to longitudinal vibration modes (ν18a and ν8a) of the *p*-phenylene rings and could thus absorb vibrational energy to be promoted to the surface of the semiconductor nanoparticles.

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Physical Chemistry **355**

## Visible Light Absorbing Commercial $TiO_2$ Powders Doped by N and C. Photocatalytic Activity Towards E. coli Inactivation and Phenol Oxidation using Solar Irradiation

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and Pulgarin, C.[a]

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[c]Russian Academy of Sciences, Institute of Problems of Chemical Physics, Moscow 142432, Russia

In recent years, broadening of the absorption spectra of $TiO_2$ has been a reason of interest in photocatalysis, since this semiconductor is only able to absorb light below 380 nm (only 2 and 3% of the light hitting the terrestrial surface). $TiO_2$ absorbing visible light can be obtained by doping the $TiO_2$ with nitrogen, carbon and sulfur [1, 2]. In this work, commercial $TiO_2$ powders (Tayca TKP 101, 102 , 103 and Degusa P-25) were ground with thiourea and then calcinated at 350 °C and 550 °C. DRS spectra showed that the absorption spectra were successful broadened to visible wavelengths, maybe due to the presence of nitrogen energetic levels located right above the valence band edge. XPS and ATR-FTIR analysis were performed in order to demonstrate that the materials were doped by nitrogen and possibly carbon. The powders calcinated at 550 °C showed a good photocatalytic activity towards E. coli inactivation when the semiconductors were illuminated by simulated solar light. Activity towards phenol oxidation will also be presented.

[1] Asahi, R., Morikawa T., Ohwaki, T., Aoki, K, Taga, Y., *Science* **2001**, 293 (5528), 269.
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Physical Chemistry **356**

## Rapid and Accurate Measurement of Residual Dipolar Couplings using a Modified *F2*-coupled HSQC Experiment

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Recent studies have shown that residual dipolar couplings (RDCs) can provide important structural insight into small organic molecules by the use of alignment media specially designed for apolar or weakly polar organic solvents [1]. The common way to extract RDCs is by measuring the difference of a coupling (line splitting) in two samples, one isotropic and one anisotropic. The splitting is usually observed in the indirect dimension (F1 coupled HSQC), but HSQC without decoupling during acquisition (*F2*-coupled HSQC) represent a more suitable strategy. The success of this experiment will crucially depend on the knowledge of the size of the heteronuclear coupling constant. If standard *F2*-coupled HSQCs show acceptable results for small dipolar couplings (<10 Hz), a major problem occurs if the range of effective couplings constants is too large: the so-called ill-defined line shapes, which result from the superposition of antiphase magnetization terms with the desired in-phase magnetization become so strong that a reliable extraction of coupling constants is not possible. In this communication, we show that a slightly modified *F2*-coupled HSQC experiment allows very fast record of perfect in-phase spectra, independently of the coupling size. The modification proposed can be very easily implemented in every type of HSQC experiment, with or without gradients, and for every type of *F1* quadrature detection. In addition, the knowledge of the range of direct couplings in the sample is not required, the influence of poorly calibrated pulses is marginal and the experiment doesn't suffer from interference due to unwanted magnetization refocusing.

[1] B. Luy, K. Kobzar, S. Knör, D. Heckmann, J. Furrer, H. Kessler, *J. Am. Chem. Soc.* **2005**, *127*, 6459.

Physical Chemistry **357**

## PHOTOCATALYTIC DECOPOSITION OF AMINO ACIDS ON $TiO_2$ STUDIED BY IN SITY ATTENUATED TOTAL REFLECTION INFRARED SPECTROSCOPY

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Adsorption and photocatalytic decomposition of several amino acids on $TiO_2$ (P25) was investigated by in situ attenuated total reflection infrared spectroscopy (ATR-IR) in a small volume flow-through cell [1][2]. The processes initiated by the photogeneration of electron/hole ($e^-/h^+$) pairs by absorption of UV light were studied. The observed reactions depend on the structure of the amino acid as well as on pH. A major species observed at the catalytic interface is oxalate. The observed adsorbed species indicate reaction pathways that were previously not considered by studies based on the analysis of dissolved species only.

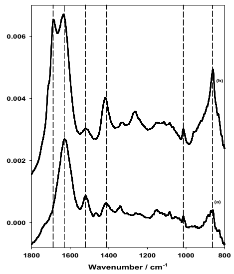

Figure 1. Two ATR-IR spectra of L-serine on $TiO_2$ are shown. The reference spectrum has been recorded in pure water over $TiO_2$. Spectrum (a) was recorded in the dark while solution of L-serine (1mM, pH= 4) was flowing over the $TiO_2$ film. Spectrum (b) was recorded after illumination. The vertical lines are just to guide the eye.

[1] I. Dolamic and T. Bürgi, J. Phys. Chem. B. **2006**, 110, 14898
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Physical Chemistry **358**

## Multilayer assemblies for light energy conversion

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Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland. *Hubert.Girault@epfl.ch

Using layer-by-layer deposition of alternate layers of polyelectrolytes and quantum dots (CdSe) on gold film electrodes, we have thin aqueous layers that can be used as modified electrodes for light energy conversion applications. Photocurrent responses originating from the CdSe sensitized ultrathin multilayer film are investigated as functions of the applied potential, the thickness of the film and the presence of quenchers in the organic phase. We also propose a theoretical model is in order to analyze the kinetics of the photoinduced electron-transfer reactions and to probe the potential distribution within the film. We shall demonstrate that we can increase the conversion efficiency of the system by building 3-Dimensional assemblies of nanoparticles. Using different kind of nanoparticles, we can reverse the electron flux from a reductive to an oxidative process.
Finally, we will study the influence of the environment (film & solution) on the lifetime kinetics of the quantum dots using time correlated single photon counting technique (TCSPC)

[1] M. Hojeij, N. Eugster, B. Su, H. H. Girault *Langmuir*. **2006**, *22*, 10652.

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Physical Chemistry **359**

## Ultraviolet and Infrared Spectroscopy of Protonated Phenylalanine in the Gas Phase

Caroline Seaiby, Jaime A. Stearns, Monia Guidi, Oleg V. Boyarkin and Thomas Rizzo

Laboratoire de Chimie Physique Moléculaire, Ecole Polytechnique de Lausanne, CH-1015 Lausanne, Switzerland.

We produce biomolecular ions in the gas phase *via* nanospray and trap them in a cooled, 22-pole ion trap where we use a variety of laser techniques to study them spectroscopically.

We have measured the electronic spectrum of cold, protonated phenylalanine, detecting the absorption by monitoring the resulting photofragmentation. Using this vibrationallly resolved spectrum, we can record the infrared-ultraviolet double resonance spectra by fixing the UV laser wavelength on a particular feature in the electronic spectrum and scanning an infrared laser. The infrared spectrum allows us to identify unambiguously features arising from different stable conformers of the molecule. The experimental results have been compared with DFT calculations, confirming the presence of two conformers.

Now that we have identified different conformers, we plan to investigate the dynamics of conformational isomerism in this small biologically related molecule. We are also adding a stage of ion-mobility selection between our nanospray ion source and our low-temperature ion trap using the technique of Field Asymmetric waveform Ion Mobility Spectrometry (FAIMS). This will allow us to perform conformational selection of biological molecules by ion mobility prior to spectroscopic interrogation.

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Physical Chemistry **360**

## Complexation of a Weak Polyampholyte with a Charged Nanoparticle.

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The conformation and titration curves of weak isolated polyampholytes are examined using Monte Carlo simulations with screened Coulomb potentials in the Grand Canonical ensemble. Two different types of monomers are considered. Depending on the solution pH, monomers A are weak acidic sites that can either be negatively charged or uncharged (as carboxylic groups) whereas monomers B are weak basic sites that can either be positively charged or uncharged (as amino groups).
The influence of the chain stiffness, primary structure and ionic concentration on the acid/base properties of the polyampholyte chains are systematically investigated. By adjusting the pH values, titration curves and then the fractions of positively ionized and negatively ionized charged monomers are calculated. Stiffness influence is estimated by comparing two models of chain: a fully flexible and a rod-like polyampholyte. We demonstrate that the primary structure plays important roles in the acid/base properties as well as the charge distribution along the polymer backbone of a statistical rod-like polyampholyte.
Phase states of the polyampholyte/nanoparticle complexes are presented and to bridge the gap with experiments, titration curves are calculated. It is shown that the presence of one oppositely charged nanoparticle significantly modifies the acid/base properties of the weak polyampholyte as well as the charge distribution along the polymer backbone.

Physical Chemistry **361**

## The optical and thermodynamic properties of the HCl hexahydrate

Simone Chiesa and Michel J. Rossi

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We present a laboratory study of the interaction of HCl with thin ice films which mimic a variety of stratospheric particles as those found in cirrus and in polar stratospheric clouds. The study is carried out at temperatures relevant for the atmosphere (170-210 K) in a high vacuum reactor. Pure ice films are grown onto a Si optical support and then exposed to a controlled amount of HCl vapor. The gas phase is monitored using a mass spectrometer, while the condensed phase is studied employing transmission FTIR spectroscopy. Two different condensates are found, depending on the doping temperature: for T<173 K the crystalline HCl hexahydrate is obtained, while for T> 173 K only an amorphous phase is formed. Mid-IR absorbances along with numerical values for the IR cross sections of the pure hexahydrate phase will be presented. The partial pressure of water over the HCl hexahydrate phase has been found to be lower by 30% than that over pure ice in the vicinity of 190 K. Values for the enthalpy of sublimation and of the activation energy for the decay of the HCl hexahydrate phase will be presented. Finally, the stability of the hexahydrate phase will be discussed, as this structure has been observed to decay into an amorphous HCl/ice system for T>195 K, with the probable formation of a quasi liquid layer on top of the film. This QLL layer is more reactive towards uptake of atmospheric gases than the crystalline phase.

[1] Chiesa S. and Rossi M. J., The IR spectroscopic and thermodynamic properties of HCl/$H_2O$ in the range 170-220 K, *article in preparation*.

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Physical Chemistry **362**

## Continuous Catalytic Hydrogenation of Organic Compounds over Pd/Amberlyst-15 in Supercritical $CO_2$

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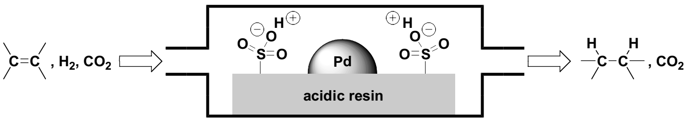
[†]Research Fellow of the Japan Society for the Promotion of Science

Palladium immobilized on a strongly acidic resin of Amberlyst-15 (denoted 1% Pd/Amberlyst-15) was synthesized by impregnation from the aqueous solution of $[Pd(NH_3)_4]Cl_2$, and applied in the continuous catalytic hydrogenation of organic compounds in supercritical $CO_2$. As test reaction, the hydrogenation of cyclohexene (**1**) to cyclohexane (**2**) was performed (conditions: 60 ºC, total pressure of 16 MPa, molar ratio **1**:$H_2$ of 1:1.8). The activity of 1% Pd/Amberlyst-15 was comparable to that of 1% Pd/C as a representative hydrogenation catalyst and much higher than that of 1% Pd/$Al_2O_3$. Other transition-metals such as Pt, Ru, and Rh were also loaded onto the resin and used for the reaction, but their activities were quite low. Note that the 1% Pd/Amberlyst-15 catalyst did not lose its high activity and selectivity for at least 12 h. The choice of a sufficiently high total pressure was found to be crucial to achieve the high catalytic performance. The reaction rate dropped drastically below a total pressure of 14 MPa, which was substantiated by phase behavior measurements. Interestingly, the dimerization of **1**, which is catalyzed by the sulfonic acid groups on Amberlyst-15, was accelerated in the pressure range 10–12 MPa, which led to a decrease in selectivity to **2**. The structure of 1% Pd/Amberlyst-15 was characterized by XAS and IR spectroscopy. Finally, 1% Pd/Amberlyst-15 was utilized in the hydrogenation of other compounds including carbonyl compounds, which will also be reported.



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Physical Chemistry **363**

## Solution Structure of $BMIM.PF_6$ in DMSO: a PGSE diffusion and NOE combined study

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The understanding of Ionic Liquid's properties is of extreme importance, especially in terms of intermolecular interactions and solution structure, for which information is lacking.[1][2][3]

1-butyl-3-methylimidazolium hexafluorophosphate ($BMIM.PF_6$) is especially suited for NMR studies as both ions have active nuclei with high receptivity. The present work consists of a NMR study that combines $^1H$ NOESY, $^{19}F,^1H$-HOESY, $^1H$ and $^{19}F$ PGSE diffusion and chemical shift analysis in $d_6$-DMSO and DMSO solutions.

NOESY data were used to determine internuclear distances and their variation with concentration. HOESY results gave information about relative ion and solvent position. DOSY experiments allowed the determination of ion mobility and radii. The combination of this data allows the description of the behavior of the IL in solution in terms of intermolecular interactions.

DOSY results indicate that at low concentrations the ions are separate and above 1:1 molar proportion (IL:DMSO) they aggregate. Inter-ionic distances obtained from computational calculations (B3PW91/6-31G** in Gaussian03) are consistent with those derived from our NMR studies, allowing the proposal of a structure for the high concentration clusters.

Experimental evidence that support the concept of a local structure similar to that found in solid state for the pure ionic liquid will be presented and discussed, as well as its variation upon dilution.

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Physical Chemistry **364**

## Investigation of Parameters Influencing *J*-couplings Across Hydrogen Bonds Using MD Simulations

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High-resolution NMR experiments contribute to structure determination of biomolecules. In addition the measurement of scalar couplings across hydrogen bonds (H-bonds) allows to identify unambiguously the donor and acceptor atom [1]. H-bonds play an important role in the stabilization and function of proteins and it is desirable to characterize them at an atomic level. On the basis of the linear combination of atomic orbitals it is possible to convert the magnitude of $^{3h}J_{NC'}$ into structural geometry [2]. It has been shown that this mere geometric dependence is in good agreement with computationally more expensive DFT calculations [2,3]. However molecular dynamics simulation ensembles and calculated *J*-coupling values from them can be further improved when NMR energy constraints are introduced [4].

Here, additional features in understanding and predicting scalar couplings from atomistic simulations are described. The sensitivity of *J*-couplings on force field parameters is considered in detail for individual couplings and depending upon the secondary structure element the atoms are involved in.

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Physical Chemistry **365**

## Adsorption and hydrogenation of chiral cinchona modifiers at catalytic Rhodium-liquid interfaces followed by ATR-IR spectroscopy.

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The importance of infrared spectroscopy (IRS) for the characterization of heterogeneous catalysts is undisputed. Information gained on the nature of the adsorbates and of their interaction with the catalytic material can be extracted from a vibrational spectrum. This has become of even more relevance in the recent past with the increasing need of studies of the surface processes under in situ conditions for a better rational design of catalysts. Attenuated total reflection (ATR)-IRS was successfully applied to study the adsorption of the chiral modifier cinchonidine (CD) on Pt[1] and Pd[2] model-catalysts, systems that are used for the enantioselective hydrogenation of activated ketones and C=C bonds, respectively. In order to understand the still debated reaction mechanism current research is focused on the design of new modifiers able to rationalize the enantioselectivity exhibited by CD as well as to the use of other metals such as Rh.

Here we show the adsorption behaviour of CD on a Rh[3] model catalyst prepared by PVD using ATR-IRS. The spectra show that in the presence of dissolved $H_2$ CD is predominantly adsorbed with the quinoline (Q) ring tilted with respect to the Rh surface. The corresponding flat adsorbed modifier (Q ring nearly parallel) is quickly hydrogenated at the anchoring group. The flat species earlier observed on Pt is considered to be involved in the enantiodifferentiation explaining the commonly lower enantiomeric excess observed in the enantioselective hydrogenation on Rh compared to that on Pt. The adsorption behaviour of CD on Rh was compared to that of β-isocinchonine, which induces superior enantioselectivity.

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Physical Chemistry **367**

## Positioning of Functional Groups on Mesoporous Silica Surfaces

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The ability to control the distribution of functional groups on mesoporous silica surfaces is crucial for advancing the potential of these materials in various fields, including drug delivery, optical applications, and catalysis. Deposition of alkoxysilane precursors from an anhydrous liquid phase is the most common postsynthetic functionalization technique. A recent study on the modification of mesoporous silica MCM-41 with aminopropylalkoxysilanes has shown that the degree of island formation and the external/internal grafting ratios are governed by the precursor reactivity and the solvent polarity [1]. The deposition of aminopropylalkoxysilanes from the gas phase opens additional possibilities for controlling the distribution of the amino groups on the mesoporous silica surface. We have investigated a method derived from Atomic Layer Deposition (ALD), with particular emphasis on the effect of the reaction temperature. Careful heat pretreatment of the mesoporous silica is essential for adjusting the amount of silanol groups [2] while maintaining the integrity of the mesoporous framework [3]. Sample characterization techniques include pore size analysis, fluorescent labeling, and DRIFTS.

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Physical Chemistry **366**

## Optical Sensing of Nanochannel Polarity

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Since the discovery of the M41S mesoporous silica family considerable effort has been directed towards the development of novel applications in the fields of catalysis, adsorption, drug delivery or sensing [1]. The tuning of specific host-guest interactions by a regulation of the nanochannel wall polarity is essential. For this purpose the functionalisation with alkoxy- or chlorosilane compounds is a powerful tool [2].

A change in the nanochannel wall properties from an initially polar to an unpolar state can be achieved by reaction of the silanol groups with chloroalkylsilanes [3]. Optical sensing of the different degrees of polarity was achieved by inclusion of fluorescent molecules featuring excited charge transfer states.

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Physical Chemistry **368**

## Millimetre wave spectroscopy and MQDT calculations of high Rydberg states of xenon

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For most atoms and molecules, the direct access to Rydberg states from the ground state requires light in the UV or VUV range. The spectral resolution is limited by the spectral bandwidth of the laser and/or the Doppler broadening. A significantly higher resolution can be obtained by combining a high-resolution laser system with millimetre radiation [1]. Such double-resonance experiments have been used to study the hyperfine structure of high Rydberg states of $^{83}$Kr [2] or ortho-$H_2$ [3].

A phase-stabilised backward wave oscillator (BWO) in the 240–360 GHz frequency range was combined with a UV laser system to record high-resolution spectra of high-$n$ Rydberg states of xenon. The millimetre wave transitions between $n$d and $n$p or $n$f Rydberg states of the isotopes $^{129}$Xe, $^{131}$Xe, and $^{132}$Xe were measured at sub-MHz resolution and detected by pulsed field-ionisation followed by mass-selective detection of the cations.

A multichannel quantum defect theory (MQDT) treatment of the hyperfine structure [4] was used to analyse the millimetre wave spectra in combination with the available data from the literature in order to obtain improved MQDT parameters and hyperfine structure parameters of the $^2P_{3/2}$ ground electronic state of $Xe^+$.

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Physical Chemistry **369**

## Unidirectional Zeolite L Antenna Material for Sensitizing Organic Solar Cells

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In device engineering, a high degree of supramolecular organization is a prerequisite for achieving desired macroscopic properties [1]. A high level of organization can be obtained by arranging zeolite L crystals as closely packed monolayers on a surface followed by subsequent insertion of strongly luminescent dyes [2]. An antenna material can be realized where the electronic excitation energy is transported in one direction only. The channel entrances of the dye-loaded zeolite L monolayer are sealed with stopcock molecules. The excitation energy is transported from the dyes inside to the surrounding material via Förster resonance energy transfer. The preparation of dye-loaded zeolite antenna monolayers opens possibilities to use dye-zeolite L materials for new types of optical devices, such as dye-zeolite sensitized organic solar cells [3].

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Physical Chemistry **370**

## VUV Spectroscopy of the high-$n$ autoionizing Rydberg states of Kr

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The autoionizing Rydberg states of Kr lie in the spectral region between the Kr $^2P_{3/2}$ and $^2P_{1/2}$ ionization thresholds in the vacuum ultraviolet. Observation of the autoionizing Rydberg series by photoionization spectroscopy to high principal quantum number $n$ allows determination of the $^2P_{1/2}$ ionization threshold of Kr by Rydberg series extrapolation. For $^{83}$Kr ($I = \frac{9}{2}$) an accurate determination of the hyperfine ionization thresholds with $F^+ = 4$ and $F^+ = 5$ is feasible if states with $n > 200$ are well resolved. In order to accomplish this, a new spectrometer for high resolution spectroscopic measurements in the VUV wavelength region has been developed based on ultra-high vacuum technology. The apparatus has been designed such as to fully exploit the FT-limited bandwidth (50 MHz) of our new solid-state VUV laser system [1]. Polar molecules in the background gas of conventional high-vacuum chambers, as well as external sources of electric and magnetic stray fields commonly restrict observation of Rydberg states to below $n \approx 200$. By optimizing the geometry of the electrodes and by reducing the background gas pressure to below $5 \times 10^{-10}$ mbar, it is possible to alleviate substantially some of the apparative limitations associated with stray electric fields within the photoexcitation region and to observe Rydberg series up to $n \gg 200$. High-resolution spectra of krypton in the autoionizing region between the $^2P_{3/2}$ and $^2P_{1/2}$ ionization thresholds have been recorded by single-photon VUV excitation. The performance and specifications of the spectrometer as well as the analysis of the spectra will be presented.

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Physical Chemistry **371**

## Metallic or oxidic palladium? Unequivocal identification of the active noble metal species in aerobic alcohol oxidation

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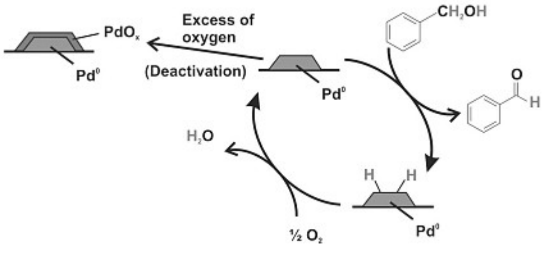
Aerobic alcohol oxidation over Pd- and Pt-based catalysts is an important process in fine chemistry and has attracted considerable attention during the past decades. However, the mechanism is still matter of discussion and an unambiguous proof of the nature of the active noble metal sites appears of fundamental importance. For this purpose, we combined *in situ* XAS for structural identification and FTIR for determining the catalytic activity online during the palladium-based alcohol oxidation in cyclohexane [1]. Our results demonstrate that palladium oxide exhibits hardly any catalytic activity for alcohol oxidation at 50 °C, while metallic Pd particles are much more active. This is in agreement with the dehydrogenation mechanism depicted in the simplified scheme below. The presented approach can be regarded as an important step forward to generally derive structure-activity relationships under dynamic reaction conditions also in liquid-phase reactions.



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Physical Chemistry **372**

## Simultaneous in situ surface and gas phase PM-IRRAS study of the NOx storage and reduction on Pt/Ba/$Al_2O_3$

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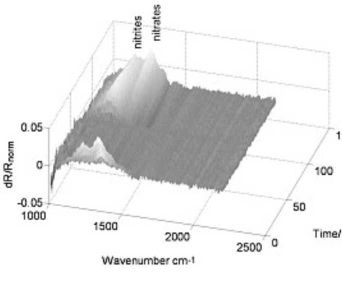
Polarization-Modulation Infrared Reflection-Absorption Spectroscopy (PM-IRRAS) is a method for simultaneous investigation of species on the catalyst surface and gas phase under pressure during reaction [1]. The method is applied to investigate the NOx storage and reduction process on Pt/Ba/$Al_2O_3$ and related systems. The catalyst powders employed are prepared by two-nozzle flame spray pyrolysis [2]. Thereby special care is taken on the effect caused by the different components in the system and their vicinity to one another (remote control). The storage and reduction processes are investigated with different reducing agents ($H_2$, CO, propene).



PM-IRRAS surface spectrum.

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Physical Chemistry **373**

## Electric field induced Linear Dichroism and polarized fluorescence of CdSe Nanodots: large anisotropy of the band-gap absorption.

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Nanocrystals of CdSe can be prepared by wet chemistry with good yields, well defined shapes, and narrow size distributions [1]. The strong confinement of the electron wave-function in these particles makes it possible to tune their optical properties, with many applications in biology, and optoelectronics. Dielectric dispersion measurements have shown that contrary to theoretical predictions, the nanocrystals have large ground-state dipole-moments [2]. We measured the electric field induced linear dichroism for a wide range of sizes of nanocrystals [3]. Large ground-state dipole-moments were indeed observed, especially for the smallest crystals. Moreover, we found that most of the dipole strength is along the direction of the ground-state dipole-moment. These results were confirmed by polarized fluorescence experiments. For the anisotropy of the bandgap absorption we propose a mechanism for intensity borrowing from intra-band transitions, induced by the field of the ground-state dipole moment.

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Physical Chemistry **375**

## Monte Carlo Study of the Importance of Physicochemical Conditions and Surface Site Distributions on the Charging Behavior of a Spherical Macroion.

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The importance of the dielectric discontinuity, ionic concentration and surface site distribution on the charging process of a spherical polyampholytic macroion have been investigated. It is well known that the electrostatic repulsions between charges on neighbouring sites tends to decrease the effective charge of polyampholyte. However, the situation is more complicated close to a dielectric breakdown since charged sites are not only interacting with neighbours but also with their own image charges and the image charges of all neighbours. Titrating site positions, ionic concentration, dielectric discontinuity and pH dependence are systematically studied using a Grand Canonical Monte Carlo method. Homogeneous, heterogeneous and patch site distributions are considered. By considering Coulomb, salt and image charges effects, results show that for different ionic concentrations, modifications of the dielectric constant of the macroion in homogeneous and heterogeneous distributions has no significant effect on the charging process of a small macroion. In that case, the reaction field counterbalances Coulomb interactions. This is not the case for the patch distributions, where Coulomb interactions are not completely counterbalanced by the reaction field. Application of the present model to pyrogenic silica is also made and compared with published experimental data obtained at different ionic concentration. A good agreement is found in the pH zone of experimental stability of pyrogenic silica (up to pH = 8.0) for all ionic concentrations.

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Physical Chemistry **374**

## Synthesis and characterization of spinel-like oxides by flame-spray pyrolysis

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Most combustion catalysts are based on supported noble metals, such as palladium, platinum and rhodium. Although highly active, these metals are expensive and often suffer from sintering or even vaporization with corresponding loss of activity. An alternative to noble metal based catalysts are mixed transition metal oxides, such as perovskites [1] or spinels [2]. However, these mixed metal oxides are commonly prepared via high-temperature routes, often leading to low-surface area materials limiting somewhat their catalytic application.

Flame-spray pyrolysis (FSP) is a versatile vapor phase synthesis method [3], ideally suited for production of high-surface area metal oxides.

This contribution will discuss the synthesis of $AB_2O_4$ (A = Mg, Zn, B = Fe, Mn, Co) mixed oxides. The activity of these materials in the catalytic combustion of methane will be reported.

[1] M. A. Pena and J. L. G. Fierro, *Chem. Rev.* **2001**, *101*, 1981.
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Physical Chemistry **376**

## Synthesis, EPR and DFT studies of a CpNi(benzenediselenolate) complex:

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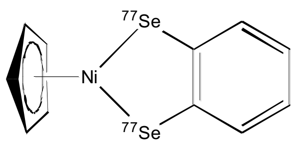
Campus de Beaulieu, 35042 Rennes Cedex, France
** Department of Physical Chemistry, University of Geneva, 30 Quai
Ernest Ansermet, 1211, Geneva, Switzerland



The synthesis of the CpNi(bds) complex (bds = 1,2-benzenediselenolate) was achieved by the method[1] of Nomura and al, using $[Zn(bds)_2](P(Ph)_4)_2$ instead of $[Ni(bds)_2](N(Bu)_4)_2$ as an intermediate. Using metallic $^{77}$Se as a precursor led to the $^{77}$Se enriched complex which was invisgated by EPR at 9 GHz and 35 GHz at variable temperature. The g and $^{77}$Se hyperfine coupling tensors were obtained from simulation of the frozen solution spectra ($g_x$= 2.1421; $g_y$= 2.1076; $g_z$= 2.0230; $T_i$= -18.0, $T_j$= -8.0 and $T_z$= 60.0). In good agreement with DFT calculations, 17% of the spin is delocalised on each selenium.

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Physical Chemistry **377**

## Oxygen Doping of Cyanine/$C_{60}$ Solar Cells

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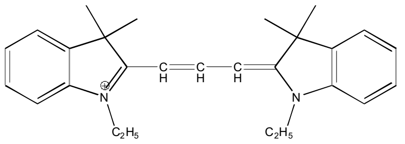
Organic semiconductors are attractive materials for low cost solar energy conversion. Cyanine dyes are ideal for the photovoltaic application for its high extinction coefficient, tunable absorption and the possiblity to form J-aggregates with highly delocalized excitons. The solar conversion efficiency of cyanine/$C_{60}$ double layer solar cells are still low, probably due to poor carrier transfer from the charge separating interface to the electrodes[1, 2]. A distinct improvement of the charge transportation in cyanine film was obtained by doping the cell with oxygen, which resulted in both high open circuit voltage ($V_{OC}$) and high short circuit current ($J_{SC}$). The overall conversion efficiency increases from 0.07% to 0.9% by doping. The current collection efficiency reached 35%.



Cyanine dye

[1] Nueesch F, Tornare G, Zuppiroli L. et al. *Sol. Energy Mater. Sol. Cell.* **2005**, *87*, 817.
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Physical Chemistry **378**

## Ultraviolet Photon-Echo for the study of protein dynamics

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Most amino-acid residues in proteins absorb in the UV below 300 nm. Using them to describe intra-protein dynamics is becoming a major goal to understand biological functions. Ultrafast experiments can deliver a high level of insight into these processes and one of the most promising methods is photon-echo. The capability of photon-echo peak shift measurements to trace band-gap correlation function has been discussed in much detail [1,2] and is widely used to investigate fluctuation dynamics of the chromophore environment .

With the final goal of studying ultrafast fluctuation dynamics in wild-type proteins by exciting the aromatic amino acid tryptophan we have implemented photon-echo technique with excitation in the UV region (at 290nm). Here, we will report the first UV photon-echo peak shift experiments on an organic dye and on tryptophan in water, using the frequency doubled output of an optical parametric amplifier as the excitation beam.

Besides being a test system for the feasibility of the experiment, the dyes are interesting for the study of non-polar solvation and internal vibrational relaxation on the femtosecond timescale, which we will present and discuss.

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Physical Chemistry **379**

## A Double Spin-Lock for Heteronuclear Multiple Quantum Coherences

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Many biological processes involve conformational rearrangements that occur on a micro-to-millisecond time scale.
Single-quantum relaxation studies can be complemented with various multiple-quantum coherence (MQC) CPMG experiments to provide a more robust measurement of the kinetics parameters and chemical shifts of the exchanging sites[1,2,3]. Such methods are adapted to study conformational exchange occurring on a millisecond time scale. On the other hand, $R_{1\rho}$ experiments give access to microsecond time scale dynamics.
Here, we present the development of a method that is equivalent to $R_{1\rho}$ experiments for multiple quantum coherences. We have designed a sequence of radio frequency (RF) pulses with alternating phases[4,5] applied on $^{15}$N and $^{1}$H simultaneously. The offset dependence in both chemical shift dimensions of the spin lock sequence has been optimized to keep multiple quantum operators invariant over a wide range of offsets.

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[2] J. Dittmer, G. Bodenhausen, *J. Am. Chem. Soc.* **2004**, *126*, 1314.
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[4] I. S. Podkorytov, N. R. Skrynnikov *J. Magn. Reson.* **2004**, *169*, 164.
[5] M. H. Levitt, R. Freeman, *J. Magn. Reson.* **1981**, *43*, 502

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Physical Chemistry **380**

## On the Role of Spins in Molecular Photoionisation: Spectroscopy and Dynamics of Autoionizing Rydberg States of ortho $H_2$

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The results of a combined experimental and theoretical investigation of the role of electronic and nuclear spins in molecular photoionization are presented. Photoionization spectra of autoionizing p Rydberg states belonging to series converging on the X $^2\Sigma_g^+$ ($v^+ = 0,\ N^+ = 3$) level of ortho $H_2^+$ have been measured in the range of principal quantum number $n = 50 - 200$. The use of a pulsed near-Fourier-transform-limited laser with a bandwidth of less than 10 MHz resulted in Doppler-limited linewidths of 25 MHz.
Below $n \approx 70$, the observed levels can be understood in terms of Hund's case (d). With increasing value of $n$, the hyperfine interactions in the core lead to a mixing of singlet and triplet characters of the Rydberg states and eventually to a complete decoupling of the Rydberg electron spin from the core spins.
Multichannel Quantum Defect Theory (MQDT) including nuclear and electron spins has been extended to treat autoionization and predict spectral intensities. The comparison with the experimental spectra has revealed a satisfactory agreement between calculated and measured line positions, linewidths and intensities and has enabled us to extract a more accurate term value for the H $^1\Sigma_g^+$ ($v = 0,\ J = 3$) level. The calculations also have been used to characterize the role of hyperfine, spin-rotational and pf interactions in rotational autoionization.

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Physical Chemistry **381**

### Quenching and recoupling of echo modulations in NMR

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Trains of spin echoes are normally modulated by homonuclear scalar couplings. It has long been known that echo modulations are quenched when the pulse repetition rates are much larger than the offsets of the coupling partners, because the spin systems behave as if they consisted of magnetically equivalent spins when the offsets are suppressed. This type of quenching of echo modulations can occur when the radio-frequency (RF) pulses are ideal, i.e., when they are perfectly homogeneous, properly calibrated to induce rotations through an angle $\pi$, and have an RF amplitude $\omega_1 = -\gamma B_1$ that is strong compared to the largest offset $\Omega_S = \omega_{0S} - \omega_{RF}$ with respect to the carrier frequency. Recently, it has been discovered that echo modulations can also be quenched when the RF pulses are non-ideal, i.e., too weak to bring about an ideal rotation of the magnetization of the coupling partners, so that the effective fields associated with the RF pulses are tilted in the rotating frame. This phenomenon typically occurs when the pulse repetition rates are much slower than the offset of the coupling partner. Under such conditions, it turns out however that for certain offsets, when the phase $\Phi_S$ due to free precession of the magnetization of the coupling partner S in the pulse interval $2\tau$ and pulse length $\tau_\pi$ approaches a multiple of $2\pi$, the echo modulations are restored.

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Physical Chemistry **382**

### Four electrode measurement of dye sensitised $TiO_2$ in photovoltaic application with Scanning Electrochemical Microscope

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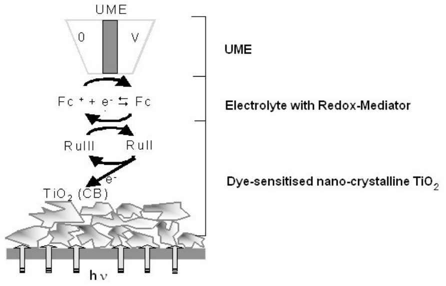
In a dye sensitized photovoltaic solar cell (DSSC), a monolayer of dye molecules is commonly adsorbed onto a nano-structured $TiO_2$ film[1]. To develop improved dyes it is important to measure the photovoltaic performance efficiently and reproducibly. We have been using a scanning electrochemical microscope[2] in combination with the contacted substrate supporting the $TiO_2$ film to test dyes and then compare with the dyes in complete assembled DSSC cells. With four electrodes it is possible to alter the potential of the anode and cathode relative to a separate reference electrode and measure photocurrents.



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Physical Chemistry **383**

### Shaped pulse Decoupling for extending the lifetimes and the bandwidth of Singlet-State NMR Spectroscopy

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In singlet-state spectroscopy, such long-lived states are generated and maintained during evolution periods that are long with respect to the spin-lattice relaxation times of the involved nuclei. The use of square pulses in decoupling sequences (such as WALTZ16 or MLEV) during this evolution interval has been shown to considerably extend the bandwidth over which long-lived states can be maintained (1).

Decoupling sequences using various shaped radio-frequency pulses have been tested to achieve the longest possible lifetimes of singlet-state populations over widest possible bandwidths, i.e., ranges of relative and absolute chemical shifts of the nuclei involved in singlet states. The use of so-called Broadband Universal Rotation Pulses for decoupling during the intervals where singlet-state populations are to be preserved allows one to extend the bandwidth by at least a factor of four with respect to the prior state-of-the-art based on continuous-wave or composite-pulse decoupling. Other approaches, including frequency-modulated decoupling sequences, appear to be less effective. The improved BURP decoupling sequences also afford an extension by a factor of ~2 of the singlet-state lifetime of aromatic J-coupled protons $H^5$ and $H^6$ in uracil, which have a chemical shift difference of 1.7 ppm (692 Hz in a static field $B_0 = 9.4$ T).The extension of the bandwidth of singlet state spectroscopy is important for applications in the study of slow exchange phenomena.

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Physical Chemistry **384**

### Demonstration of a three-dimensional Rydberg atom trap

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Recent progress in the development of methods by which to decelerate and manipulate the translational motion of Rydberg atoms and molecules in the gas phase using static and time-varying inhomogeneous electric fields has led to the experimental realisation of Rydberg atom optics elements including a lens [1], a mirror [2] and a two-dimensional trap [3]. These experiments exploit the very large electric dipole moments associated with Rydberg Stark states, and have demonstrated the possibility to stop a seeded, pulsed, supersonic beam of atomic hydrogen travelling with an initial velocity of 700 $\mathrm{ms}^{-1}$ within 3 mm ($\sim 5\ \mu$s) using electric fields of only a few $\mathrm{kVcm}^{-1}$.

With the goal of achieving complete control of a cloud of Rydberg atoms or molecules in three-dimensions, we have recently designed and constructed a three-dimensional electrostatic trap for these particles. The design of this trap will be presented along with the results of a series of experiments in which we have used the trap to confine, in three dimensions, a cloud of atomic hydrogen Rydberg atoms in states with principal quantum numbers around $n = 30$. The dynamics of the Rydberg atoms in the trap have been investigated by pulsed field ionisation and imaging techniques. Under favourable conditions, trapping times on the order of 150 $\mu$s have been observed.

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Physical Chemistry **385**

## Investigations of the rovibrational structure of the $\mathrm{Xe}_2^+$ ionic levels

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Pulsed-field-ionisation zero-kinetic-energy (PFI-ZEKE) photoelectron spectra of $\mathrm{Xe}_2$ were measured in the range of $107100\,\mathrm{cm}^{-1}$ to $108200\,\mathrm{cm}^{-1}$ where the lowest vibrational levels of the II(1/2u) and the II(1/2g) states are located [1]. Using a two-photon excitation scheme via a vibrational level of the C $0_\mathrm{u}^+$ state, the rotational structure of the ionic levels have been analysed [2].

The measurements were performed using a high resolution VUV laser system [3] to excite a single rovibrational line of the C $0_\mathrm{u}^+$ $(v', J') \leftarrow$ X $0_\mathrm{g}^+$ $(0,\ J'')$ transition in $\mathrm{Xe}_2$ [2], followed by a further excitation to very high Rydberg states ($n \approx 300$) located just below the ionisation thresholds associated with the rovibronic states of $\mathrm{Xe}_2^+$. These Rydberg states were then field ionised using a high resolution electric field pulse sequence to monitor the yield of electrons as a function of the excitation wave number at a resolution of better than $0.1\,\mathrm{cm}^{-1}$ [4].

This work is financially supported by the ETH Zürich and the Swiss National Science Foundation.

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Physical Chemistry **387**

## Catalytic Chiral Metal Surfaces Generated by Adsorption of *O*-phenyl Derivatives of Cinchonidine

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Chirally modified platinum surfaces generated from the adsorption of *O*-phenyl derivatives of cinchonidine, bearing different substituent at the phenyl ring, shows interesting enantioselective properties in the heterogeneous enantioselective hydrogenations of α-activated ketones.[1] It has been observed[2] that *O*-phenyl-cinchonidine (PhOCD) and *O*-(3,5-dimethylphenyl)-cinchonidine (dMePhOCD), afford the (*S*)-enantiomer, despite having the same absolute configuration as cinchonidine (CD) that yields the (*R*)-enantiomer. On the contrary, *O*-[(3,5-bis-(trifluoromethyl)-phenyl]-cinchonidine inverts again the sense of enantioselection, yielding the (*R*)-enantiomer as CD. The adsorption behaviour of the modifiers and the structure of the resulting chiral solid-liquid interface have been investigated combining attenuated total reflection (ATR) infrared spectroscopy with density functional theory (DFT) calculations. The results of the conformational study of each adsorbed modifier reveal a correlation between the spatial orientation of the substituted phenyl rings and the enantioselectivity of the catalyst. Spectroscopic experiments and theoretical calculations support an interpretation according to which the displacement of the phenyl rings reshapes the surface chiral site formed by the adsorbed modifiers, thus generating surfaces with different enantiodifferentiating properties.

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Physical Chemistry **386**

## Distinguishing Sequence- and Conformation-Specific Peptide Structural Motifs by Electron Transfer Dissociation Mass Spectrometry

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Rapid development of gas-phase biomolecule fragmentation techniques has significantly advanced mass spectrometry-based peptide and protein structural analysis. Improving both the efficiency and the complementarity of the existing fragmentation methods for peptide sequencing and relative quantitation of PTMs, as well as learning the insights into higher order peptide and protein structures are among the current challenges of tandem mass spectrometry. Here, we attempt to meet some of these challenges by monitoring radical intermediate lifetimes in electron transfer dissociation (ETD).

Experiments were performed on a Paul ion trap mass spectrometer (HCT Ultra, Bruker Daltonics, Bremen, Germany) equipped with simultaneous CID and ETD. Standard and synthetic peptides were electrosprayionized using a microfluidic chip-based interface (Agilent, UK).

Preliminary data indicate a sequence-dependent efficient separation of short and long lifetime radical intermediate complexes in ETD. Monitoring radical complexes lifetime as a function of ion internal energy provides additional information on peptides gas-phase conformations. The correlation with amino acid properties is under consideration to account for the differences in radical intermediate lifetimes. Both targeted and statistical analysis against a peptide library are currently undertaken to achieve method validation and indicate its advantages over available electron capture dissociation (ECD)-based approaches, particularly double resonance and cold Penning ion trap ECD. Improved fundamental understanding of gas-phase radical ion chemistry during ETD should provide a basis for product ion abundance integration into proteomics database searches, facilitate *de novo* peptide sequencing and increase the reliability for relative quantitation of PTMs.

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Physical Chemistry **388**

## Observation of Photogenerated Nascent Aqueous Iodine Radicals via X-Ray Absorption Spectroscopy

Van-Thai Pham[1], Wojciech Gawelda[1,2], Chris Milne[1,2], Maik Kaiser[1,2], Amal Elnahhas[1], Renske Van der Veen[1,2], Yuri Zaushitsyn[1], Daniel Grolimund[2], Steven L. Johnson[2], Rafael Abela[2], Christian Bressler[1] and Majed Chergui[1*]

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Sovation dynamics includes the structural rearrangement of solvent molecules around a photoexcited solute on the femtosecond time scale. We are implementing time-resolved X-ray absorption spectroscopy as a tool to monitor such rearrangements in real time, currently with 50ps time resolution, but soon with 100fs resolution at microXAS beamline of the Swiss Light Source. Photodetachment of an electron from aqueous iodide leads to formation of a short-lived atomic radical in solution. We have followed the birth and decay of iodine radical with ps XAFS as well as with fs laser spectroscopy. The analysis towards an ultrafast partial back transfer of an electron from the caging water molecules to a nascent iodine, which is supported by both spectroscopic tools. This is currently being modeled with time dependent DFT simulation. Implication towards liquid phase chemistry and future experiments exploiting fs X-ray will be discussed.

We can also detect the formation of $I_2^-$, $I_3^-$, in solution on the time scales, which is consistent with their published rate constants.

A careful analyzing of laser and X-ray data is in progress. Their supplementation to each other will help us understanding better solvation dynamics in aqueous iodide.

Physical Chemistry **389**

# Electronic structure of ionic liquids by HeI photoelectron spectroscopy

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The interest in room-temperature ionic liquids (ILs), consisting of an organic cation and inorganic anion, has recently been raised due to their properties such as wide temperature range in the liquid phase, excellent chemical stability at RT, very low vapor pressure and high heat capacities [1,2].

We investigated the electronic structure of a series of ILs deposited onto a graphite film with a HeI photoelectron spectrometer (PES).

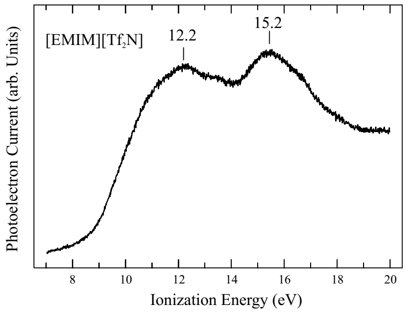

**Fig 1**. PES of [EMIM][Tf$_2$N]

For [EMIM][Tf$_2$N] (Fig.1) the signal extends from 8 to 19 eV, with two broad peaks at 12.2 eV and 15.2 eV, in agreement with ref. [3]. The signal was largely unstructured for the other ILs studied.

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Physical Chemistry **390**

# High-Resolution Photoelectron Spectroscopy Study of the Energy Level Structure of ArXe$^+$ and KrXe$^+$

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Heteronuclear rare gas ions ArXe$^+$ and KrXe$^+$ possess six low-lying electronic states which are labeled as X(1/2), A$_1$(3/2), A$_2$(1/2), B(1/2), C$_1$(3/2) and C$_2$(1/2). The potential curves of the X and A states dissociate to Xe$^+$ ($^2P_{3/2,\,1/2}$) + Y ($^1S_0$), and those of the B and C states to Y$^+$ ($^2P_{3/2,\,1/2}$) + Xe ($^1S_0$), where Y is either Ar or Kr. Only limited information is available on these states [1-3].

The pulsed-field-ionization (PFI) zero-kinetic-energy (ZEKE) photoelectron spectra of several vibrational levels of the lowest three electronic states of KrXe$^+$ have been recorded via the $0_u^+$ and 1 intermediate states correlating to the Xe$^*$ ($[5p]^5 6s'[1/2]_1$) + Kr ($^1S_0$) dissociation limit. The vibrational levels of the higher lying B and C$_1$(3/2) states could only be observed following excitation via a Rydberg state associated with the Kr$^*$ ($[4p]^5 5s'[3/2]_1$) + Xe ($^1S_0$) dissociation limit. The vibrational structures of the lowest three electronic states of ArXe$^+$ have been measured via the $0_u^+$ and 1 Rydberg states correlating with the Xe$^*$ ($[5p]^5 6s'[1/2]_1$) + Ar ($^1S_0$) limit.

The experimental information has been used to derive potential curves for these states. To this end, a potential model was developed which treats all the six curves globally and includes the effects of long-range interactions as well as the charge exchange interaction and the spin-orbit interaction. The potential parameters have been determined in a least square fit to the observed levels.

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Physical Chemistry **391**

# REMPI of formaldehyde

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We present a three-colour resonance-enhanced multi-photon ionisation (REMPI) study of formaldehyde. In a first experiment, the 3p$_x$ Rydberg state of CH$_2$O was excited via selected rotational states of the $2^1 4^3$ vibrational level of the $\tilde{A}\ {}^1A_2$ first excited electronic state and subsequently ionised with a third photon. The rotationally resolved spectra of the vibrational ground state and two vibrationally excited levels of B$_1$ and B$_2$ vibronic symmetry (the $4^1$ and $6^1$, respectively) of the 3p$_x$ state are presented.

In a second experiment, single rovibrational levels of the 3p$_x$ intermediate state were selected and pulsed-field-ionisation zero-kinetic-energy (PFI-ZEKE) photoelectron spectra of the $\widetilde{X}^+\ {}^2B_2\ 0^0$, $4^1$ and $6^1$ states were recorded. The intensities of the rotationally resolved photoelectron spectra could be modelled using the orbital ionisation model described in Ref. [1].

Rotational constants for the 3p$_x$ and $\widetilde{X}^+$ states and the first adiabatic ionisation energy of CH$_2$O have been determined. The results are compared to those obtained in previous studies of CH$_2$O by REMPI [2] and single-photon PFI-ZEKE photoelectron spectroscopy [3].

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Physical Chemistry **392**

# Block copolymer vesicles as carriers and biological membrane mimetics

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Amphiphilic block copolymers aggregate in water forming different morphologies [1]. The interest in vesicular structures arises from the potential applications in different fields like delivery-release or nanoreactors [2].

By combination of different techniques like NMR, GPC, DLS, FCS, LB, BAM and TEM, we investigated the ABA block copolymers (A – polyoxazoline**,** B - polydimethylsiloxane) concerning the composition and self-assembly of into vesicular and giant vesicular structures.

The aim of this study was to obtain quantitative information on membrane properties, in particular, the intramembrane lateral diffusion. Such observations are feasible with the fluorescence correlation spectroscopy after the polymer chains had been covalently labeled [3]. This approach will be further applied to investigate protein-reconstituted polymer membranes [4] to understand the structural details of such a matrix perturbed by a thickness-mismatch like a membrane protein.

This poster will present the synthesis, purification and characterization of the amphiphilic ABA copolymers, as well as systematic studies of self assembly into planar and spherical membranes, and polymer diffusion

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Physical Chemistry **393**

## PFI-ZEKE spectroscopy of the lowest electronic states of the $\mathrm{ArKr}^+$ ion

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We persent a photoionization and PFI-ZEKE photoelectron spectroscopic study of the ArKr mixed rare-gas dimer. The ground state of the dimer is almost repulsive ($D_e \approx 116$ cm$^{-1}$ [1]), but in some excited neutral and ionic states the dimer are strongly bound [2-4]. The Rydberg and ionic states were accessed in a resonant two-photon (VUV + VIS) excitation in the wavelength range 108000-113000 cm$^{-1}$ via intermediate low-*n* Rydberg states corresponding to Ar($^1$S$_0$) + Kr(5p) and Kr($^1$S$_0$) + Ar(4s) dissociation limits. The potential curves of the ion were derived from the positions of vibrational bands observed in the PFI-ZEKE photoelectron spectra. Information on the vibrational structure of the intermediate low-*n* Rydberg states could also be obtained and absolute vibrational assignments derived from an analysis of the isotopic shifts of the vibrational bands.

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Physical Chemistry **394**

## Spectroscopic characterization and potential curves of $\mathrm{Ne}(^1\mathrm{S}_0)+\mathrm{Ne}(4\mathrm{p}')$ autoionizing states

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We persent a study of the electronic and vibrational autoionization and the predissociation dynamics of Ne$_2$ Rydberg states located below the dissociation limit of the I(1/2u) electronic ground state of $\mathrm{Ne}_2^+$. The Rydberg states were accessed in a resonant two-photon (VUV+UV) excitation from the X $0_g^+$ electronic ground state [1] of Ne$_2$ via the C $0_u^+(v'{=}1$ and 2) [2] intermediate levels. The intermediate state has two potential minima, and the vibrational wavefunctions of the $v'$=1 and 2 levels are localized at different internuclear distances, enabling distinct regions of the potential energy curves of the autoionizing and predissociationg Rydberg states to be accessed. The spectrum of the autoionizing states was recorded in the wavelength range 162000-172000 cm$^{-1}$, which corresponds to $n^* \approx$ 3-6. Rotationally resolved spectra of $1_g$ and $0_g^+$ states of $^{20}\mathrm{Ne}_2$ and $^{20}\mathrm{Ne} -^{22}\mathrm{Ne}$ near the Ne(2p$^6$ $^1$S$_0$) + Ne(2p$^5$4p′) dissociation limit allowed us to make an absolute vibrational assignment of the spectra. A potential model similar to that introduced by Lipson and Field [3] was employed to reconstruct the interaction potentials. The potentials contain a significant potential barrier originating from a repulsive interaction of the Rydberg electron with the neutral atom. The accuracy of the potential curve in the potential well region (2-8 Å) was found to be better than 5 cm$^{-1}$.

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Physical Chemistry **395**

## Vibrational Spectra and *Ab initio* Calculations for the Study of Intramolecular Vibrational Redistribution in the CH-chromophore in $\mathrm{CHD_2I}$

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Intramolecular vibrational energy redistribution (IVR) is a central primary process in unimolecular chemical reaction dynamics. There are two main approaches towards its understanding. One is the analysis of the highly resolved vibrational spectra of polyatomic molecules [1,2] sometimes combined with *ab initio* calculations. Another approach consists in time resolved femtosecond (fs) pump-probe experiments, which we have recently carried out for a series of alkyliodides [3] including CHD$_2$I. In the present work, the infrared absorption spectrum of CHD$_2$I has been recorded with a Bomem Fourier transform infrared spectrometer from 500 to 12000 cm$^{-1}$. Vibrational variational calculations were based on a 3-dimensional *ab initio* potential energy and electric dipole moment surface in normal coordinates. The anharmonic resonance structure between the CH-stretching and bending modes was investigated via an effective Hamiltonian. Finally, we have derived the time dependent dynamics on the fs time scale [4].

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Physical Chemistry **396**

## Parity violation and tunneling stereomutation in HSSCl and HSSCN and their isotopomers, other disulfides and sulfoxides

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Spectroscopic experiments to detect and measure quantitatively the small parity violating energy difference $\Delta_{PV}E$ between the enantiomers of chiral molecules constitute an important frontier at the interdisciplinary boundary between chemistry and high energy physics [1-3]. We have recently shown that ClSSCl [4] and ClOOCl [5] are two examples of very simple chiral molecules, for which the dynamics in the ground state are dominated by parity violation. In particular ClOOCl is of interest, as it is predicted to show tunneling switching at modest excitations around 1000 cm$^{-1}$. In a search for further, related systems we have studied tunneling switching and parity violation in the elusive compounds HSSCl and HSSCN and their deutero isotopomers by *ab initio* calculations. We show that these compounds as well have properties that are, in principle, suitable for experiments on molecular parity violation. We report further work on related compounds such as other disulfides and sulfoxides.

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Physical Chemistry **397**

### Improvements on a pulsed slit jet-cavity ring down experiment

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Cavity ring down spectroscopy with a continuous wave laser is an interesting technique since it allows direct measurements of absorbance, very high resolution and extreme sensitivity [1-4]. When it is combined with pulsed supersonic slit jet expansion, it reduces Doppler broadening, and pressure broadening and congestions arising from vibrational and rotational hot bands are largely removed. The assignment of highly resolved spectra is simplified. The combination of these two techniques has successfully been developed in our group to measure combination bands of nitrous oxide, chloroform, and methane [1, 2]. The trigger system uses a simple passive scheme, where the cavity length is periodically changed so that the cavity length matches the laser wavelength [1-3]. Our techniques have also been recently successfully adopted by other groups [5-6].

Here we present new improvements on the apparatus in our laboratory. Both the trigger system and the jet expansion have been optimized to allow better quantitative measurements. Also the development of a new data acquisition is in progress: it controls all the instruments, allows a regulation of the jet expansion in the cavity and increases the signal to noise ratio. We shall report on the experimental aspects of these developments and on results of ongoing experiments.

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### Global Analysis of $CH_4$ Lines in the 0-3200 $cm^{-1}$ Region

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We have carried out new measurements of infrared spectra of the spherical top molecules $^{12}CH_4$, $^{13}CH_4$ and $^{12}CD_4$ at low temperature (80K) and at very high resolution (0.0027 $cm^{-1}$ for spectra in the pentad region around 2900 $cm^{-1}$) using the Zürich prototype Bruker 125 spectrometer (ZP 2001) [1] combined with a low temperature cooling cell [2]. Due to low temperature, the Doppler full width at half maximum was reduced by a factor of 1.91 to 0.0045 $cm^{-1}$ in the pentad region. We report the global analysis of $^{13}CH_4$-transitions up to 3200 $cm^{-1}$ and compare to previous work [3]. In the present work line positions are reproduced with an rms deviation of 0.0009 $cm^{-1}$. The complex interacting system is analyzed using an effective Hamiltonian theory described in [4]. We also discuss an introduction into the tensorial formalism [5].

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### Block Copolymer Self-Assembly Involving Competing Length Scales

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Self-assembly in block copolymer-based systems resulting in hierarchically ordered structures characterized by two different length scales have been realized in several systems during the last decade. These systems usually involve three chemically different moieties and in combination with a polymer chain architecture that involves two different length scales, e.g. a diblock copolymer consisting of a linear homopolymer block and a comb copolymer block, the formation of such structures is quite obvious. When aiming at structure formation involving a genuine competition between different length scales we need to restrict ourselves to binary block copolymers, i.e. block copolymers involving only two chemically different moieties, with a molecular architecture characterized by two length scales. The simplest example consists of linear $A_m$-*b*-(A-*b*-B)$_n$-$B_m$ symmetric multiblock copolymers. Here A and B represent chemically different “short” flexible chains of equal length. The parameters *m* and *n* denote the length of the end blocks and the number of symmetric A-*b*-B diblocks of the middle multiblock respectively.

Interesting new phenomena that occur within the (*m*, *n*)-parameter space include: a homogeneous melt characterized by a small angle X-ray scattering pattern with two scattering peaks, complex self-assembled structures characterized by two different length scales, several self-assembled structures with the cubic symmetry, i.e. face-centered cubic, body-centered cubic, simple cubic and “single” gyroid, and a variety of order-order transitions between different ordered structures involving a large and discontinuous change in the periodicity length scale. These results demonstrate that this new class of materials should have great potential in the area of responsive nanomaterials, e.g. temperature switching functional properties.

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### Mesoscale dynamics in nanostructured polymeric fluids

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With tapping mode scanning force microscopy we observe the microdomain dynamics at the surface of thin films of block copolymer melts and concentrated solutions. A high image acquisition rate and the correction of image distortions with non-linear registration techniques enable a new view onto fundamental processes of structure formation in melts and concentrated solutions of block copolymers and multi-component polymeric fluids. One example is the structural phase transition from cylinders to a hexagonal perforated lamella in a thin film of a concentrated solution of polystyrene-*block*-polybutadiene-*block*-polystyrene in chloroform [1]. From the kinetics of the phase transition we could estimate the interfacial tension between the two differently ordered fluids. Other experiments show correlations between the dynamics of neighboring defects [2], annealing of defects via formation of transient phases [3], shape fluctuations of cylinders [3,4] and lamellae [4], as well as the dynamics of individual perforations in a hexagonally perforated lamellae [4].

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