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Physical Chemistry **PC 1**

Correlated motions in biomolecules by HDR NMR spectroscopy

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Protein function is often related to internal dynamics occurring on µs-ms timescales, that can give rise to chemical exchange contributions to NMR relaxation. In a heteronuclear two-spin system, correlated motions of the two nuclei induce cross-relaxation between multiple-quantum coherences that can be quantified using new Heteronuclear Double Resonance (HDR) techniques [1]. An analytical model describes the effect of an applied rf field on the relaxation rate of interest in the presence of fast exchange [2], providing accurate information on the kinetics of correlated processes. We show that motions on similar timescales are present in the two different bonding surfaces in human ubiquitin and in the linker between them (Phe45), suggesting the presence of a possible global motion. Additional applications of HDR give insights into the dynamics undergoing in the KID-binding domain (KIX) of CBP. We identified the presence of exchange processes, faster than the one reported in [3], outside the main helices of KIX. These motions are most likely the sign of conformational disorder within the native state, which may promote the transition to the unfolded ensemble.

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Physical Chemistry **PC 3**

Multiple-scattering analysis of the time-resolved XAS spectra of ligated Myoglobin in physiological media

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Myoglobin (Mb) is one of the best characterized metalloproteins, its main function being the facilitation of oxygen diffusion on muscle cells. Understanding the mechanism by which Mb discriminates between ligands has been the subject of many studies over the past years. Despite the wealth of information available from numerous experimental and theoretical studies, a microscopic description of ligand detachment and rebinding remains elusive, and fundamental questions are still to be answered. Of particular interest is the study of NO rebinding to Mb. The recombination of the NO molecule to myoglobin is thought to have two geminate phases near room temperature [1]. Following ultrafast photodissociation in the aqueous phase near room temperature, the NO molecule geminately recombines within 100 200 ps, which is much faster than in the case of CO.

X-ray Absorption Spectroscopy (XAS) is a suitable experimental technique to probe local and electronic structures in disordered media - on which most of the relevant chemical and biological process occur. The low-energy part of the XAS is of great interest for bio-chemical studies since it is extremely sensitive to the geometrical and electronic structure of the absorbing site. We used the MXAN code [2] to perform fits on the XAS spectra of different forms of ligated Myoglobin in physiological media, both before and after photoexcitation. The fits were done by changing the structural parameters of the site around the iron atom, *i.e.*, the heme, the ligand and the distal and proximal Histidines. Our results are in close agreement with the structures determined by x-ray crystallography, showing the power of the technique in determining local structures of proteins in physiological conditions.

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Physical Chemistry **PC 2**

Xanthene dyes as a dynamic probe for hydrogen-bonding properties at liquid interfaces: time-resolved second harmonic generation study

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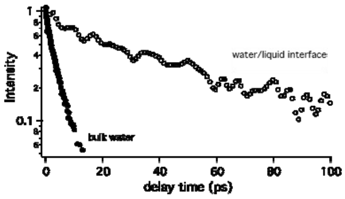
The excited-state dynamics of Eosin B (EB), a xanthene dyes family representative, was investigated with polarization-dependent and time-resolved surface second harmonic generation at liquid/water interfaces.[1] It was found that the change of the sample parameters such as concentration, age of the sample, and nature of the organic phase as well as the shortening of the excited-state lifetime of EB could be attributed to the formation of EB aggregates adsorbed at the interface. Moreover, the excited-state lifetime of EB at liquid/water interfaces is much longer than in bulk water, where the excited-state population undergoes ultrafast hydrogen bond assisted nonradiative deactivation within picoseconds.[2]



Excited-state dynamics of EB in bulk water and at liquid interface.

The strong increase of the excited-state lifetime of EB at liquid/water interfaces opens favorable prospects of applying this molecule as a fluorescence interfacial probe.

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Physical Chemistry **PC 4**

Light management in dye-sensitized solar cells

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Dye-sensitized solar cells (DSCs) are a promising low-cost alternative to conventional *p-n* junction photovoltaic devices. Improving light harvesting and the resulting photocurrent while maintaining the photovoltage is one of the key factors to reach higher efficiencies in DSCs beyond that of the current state-of-the-art [1]. We present two different strategies to achieve this goal. The first consists of using sub-micrometer sized mesoporous beads of TiO_2 that combine the advantage of light scattering without sacrificing dye loading. Such structure considerably increases the red response of DSCs and has resulted in power-to-current conversion efficiencies over 11% [2]. The second approach makes use of the light scattering and light concentration properties of plasmons excited in metal nanoparticles. Owing to their high scattering cross-section and local field enhancement they offer great potential to improve light harvesting in thin film photovoltaics [3]. Herein we present the latest results on the experimental implementation of plasmonic nanoparticles in DSCs and analyze their impact on the DSC characteristics in general and on light harvesting in particular.

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Physical Chemistry **PC 5**

Chemical reactions at ultralow temperatures: charge transfer and radiative processes in the Ca^+ + Rb system.

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A new experiment for the study of chemical reactions between atomic and molecular ions and atoms at very low temperatures ($T \approx 10$ mK) has been conceived and developed, allowing to probe the dynamics of ion-neutral chemical processes at collision energies two orders of magnitude lower than previously investigated [1]. The present experiment aims at exploring chemical phenomena in a new physical regime, validating low temperature ion-neutral reaction models [2], and studying quantum effects in very cold collisions. Cold ions are produced by laser and sympathetic cooling in a linear rf quadrupole trap. Ultracold atoms are generated using laser cooling in a magneto-optical trap.

The results of the test reaction ^{87}Rb + $^{40}Ca^+$ are presented. It is found that the ionic products of this reaction are (i) Rb^+ *via* a non-adiabatic crossing of entrance and charge transfer potential energy curves, and (ii) $CaRb^+$ *via* a radiative process. To our knowledge, this is the first experimental observation of the formation of a molecular ion at ultralow temperatures stabilized by the emission of radiation, and opens the door to new studies of this class of reaction. The state and temperature dependence of the rates of the above processes are investigated. Prospects for future investigations in the light of these results, in particular the use of sympathetically cooled state selected molecular ions as a reactant, are also highlighted.

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Physical Chemistry **PC 6**

DYNAMICAL PROCESSES IN RYDBERG STARK DECELERATION AND TRAPPING

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The development of methods to decelerate and manipulate the translational motion of Rydberg atoms and molecules in the gas phase using static and time-varying inhomogeneous electric fields [1] has led to the experimental realization of Rydberg atom optics elements including a lens [2], a mirror [3] and two- and three-dimensional traps [4,5]. These experiments make use of the very large electric dipole moments associated with Rydberg Stark states. Recently, we have demonstrated the deceleration of a seeded, pulsed, supersonic beam of hydrogen atoms with an initial velocity of 600 m/s followed by a rapid, adiabatic 90° deflection and subsequent electrostatic trapping within approximately 25 μs using pulsed electric fields of a few kV/cm [6]. In experiments in which the Rydberg atoms and molecules are trapped, trap losses can arise from transitions induced by blackbody radiation, from collisions between the trapped Rydberg atoms, or collisions with the background gas. We have shown that the dominant trap loss mechanism in hydrogen atom trapping experiments is blackbody-radiation-induced ionization at room temperature and at $T \approx 125$ K. To quantify trap loss processes other than blackbody-radiation-induced transitions, an experimental setup which can be operated at 4 K has been developed and first measurements will be presented.

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Physical Chemistry **PC 7**

High-resolution spectroscopy and intramolecular vibrational energy redistribution (IVR) in methyliodide isotopomers

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In our group we investigate the methyl iodide isotopomers (CH_3I, CH_2DI and CHD_2I) and the corresponding acetylenic compounds IH_2C-CCH as prototypes for the Intramolecular Vibrational energy Redistribution (IVR) [1-2]. On one hand, the time-resolved approach using fs-pump-probe experiments has revealed different relaxation time scales (from fs to several 100 ps) to the CI mode after excitation of the first overtone of the CH-stretching modes. On the other hand, the frequency-resolved approach using highly-resolved FTIR spectroscopy provides complementary information, such as the coupling schemes between the vibrational states. The understanding of all the couplings makes it possible to build an effective and finally a real Hamiltonian, to which the application of time-dependent quantum dynamics should reproduce the relaxation times observed experimentally [3].

In a recent investigation regarding CHD_2I, we have found that at least two dark states interact with the CH-stretching mode but a complete assignment was not possible because of the weakness of the coupling and the reduced number of data [2]. Here we focus on the same region of another isotopomer, *i. e.* CH_2DI and present our most recent results.

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Physical Chemistry **PC 8**

Cold ion spectroscopy of FAIMS-selected conformations of biomolecules

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A major source of the congestion in the electronic spectra of gas-phase biomolecules arises from the presence of a number of stable conformers, even at the low temperature attainable in a cold, radio-frequency ion trap[1]. In order to simplify the spectrum, we make use of Field Asymmetric-waveform Ion Mobility Spectrometry (FAIMS)[2] to separate the gas phase conformers of biomolecules before introducing them into the cold trap, where they are interrogated with photofragment spectroscopy. We show that the dense electronic spectrum of [bradykinin+2H]$^{2+}$ can be decomposed into contributions from different conformational families, proving the feasibility and advantages of the marriage of ion mobility with cold ion spectroscopy[3]. The coupling of the two techniques can also provide insight into the conformational distribution of biomolecular ions in the gas phase and its connection to the liquid phase distribution.

We also present photofragment electronic spectra of various charge states of ubiquitin, a small protein of 76 amino acids. The spectra exhibit sharp features, indicating that molecules of this size can be cooled in the environment of the cold ion trap. Some preliminary results of conformer-selected electronic spectra of ubiquitin using FAIMS will also be shown.

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Physical Chemistry **PC 9**

Laser induced pH jumps and pH equilibration.

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Commonly proton transfer reactions, including acid-base recombination, are considered “nearly instantaneous” thanks to the Grotthuss proton diffusion mechanism. However, their actual time scales may stretch far into the microsecond ranges as the effective rate of the bimolecular neutralization reaction depends critically on the actual concentrations of protons and bases. In modern experiments optically triggered rapid proton release, pH-jumps, is often applied to study kinetics of pH dependent processes (protein folding, proton transfers, etc). Description of how free protons are delivered and distributed after pH jumps is critical to avoid confusions between kinetics of the examined process and solution equilibration.

o-Nitrobenzaldehyde (oNBA) is a well researched and commonly used proton cage molecule. Despite this, many details regarding its photoreaction (i.e. time scale of the proton release) remained controversial. Transient pump-probe IR spectroscopy (TR-IR) and ab initio molecular dynamics (AIMD) were used to study the mechanism of the oNBA transformation[1] and the dynamics of the resulting pH-jump[2]. Spectroscopic and AIMD data shown that the reaction follows a two step mechanism with a ketene intermediate (7ps lifetime). Finally the proton dissociated of the carboxylic end product with a time constant ~20ns[1]. Its further fate was investigated with acetate ions as an IR proton sensor. The aqueous solution undergoing the pH jump revealed highly complex, kinetically controlled behavior[2] and reached highly counterintuitive states. Initially, acetate ions (pKa 4.8) were observed protonated in presence of OH^- (pKa 15.7) for hundreds of nanoseconds. Within that time parameters such as pKa, pKb, pKw didn’t provide insight into the acid-base system.

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[2] Paper in preparation M. L. Donten, P. Hamm

Physical Chemistry **PC 10**

Probing the Influence of Electrolyte on the Charge Carrier Generation Dynamics in DSSC using THz Time-Domain Spectroscopy

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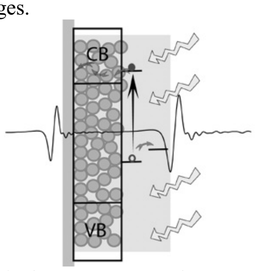
The dye sensitized solar cell represents the promise of a cheap and effective alternative to standard silicon based solar cells in the search of alternative energy sources[1]. The functioning of those devices is based on a kinetic competition of the injection of the electron from the sensitizer into the conduction band of the semiconductor, the recombination of the electron with the oxidized dye, the regeneration of the dye by and electrolyte and the extraction of the charges.



We have used Optical-Pump THz-probe spectroscopy[2] to investigate the injection kinetics of electrons into the conduction band of TiO_2. As THz-TDS is a technique sensitive to the generation of free charges and the type of transport, it gives complementary information to transient absorbance measurements.

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Physical Chemistry **PC 11**

Quantum-state Resolved Studies of the Physisorption and Chemisorption of Water

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The condensation probability of water molecules on solid ice is an important parameter in the modeling of polar stratospheric cloud formation and is therefore needed in the prediction of ozone depletion in the stratosphere. The sticking of water on metal surfaces plays an important role in corrosion processes and in catalysis. Previous molecular beam experiments have measured H_2O sticking coefficients on ice and metal surfaces as a function of incidence energy and angle but the role of selective vibrational and rotational excitation of the incident water molecules in physisorption or chemisorption reactions has never been investigated until now.

In our study, we combine a molecular beam/surface science apparatus with a powerful continuous wave (cw) infrared laser to investigate the influence of selective vibrational excitation on the physisorption of D_2O on amorphous D_2O-ice and on the chemisorption of D_2O on a Ni(111) surface. Water molecules are excited to specific ro-vibrational states with one quantum of O-D stretch by cw laser excitation in a molecular beam before they collide with defined speed and incident angle with the solid surface in ultrahigh vacuum. Physisorption probabilities are measured by a mass spectrometer using a modulated beam reflection technique based on the King and Wells method. Dissociative chemisorption probabilities are quantified using Auger electron spectroscopy to detect surface adsorbed oxygen.

Laser preparation of different vibrational modes of water enables us to probe for mode specificity in its physisorption and chemisorption. The results of our studies will help to clarify the role of vibrational energy transfer in the sticking and reaction of water on ice and metal surfaces and will contribute to a detailed predictive understanding of these important processes.

Physical Chemistry **PC 12**

Dynamic structure of supported gold in liquid phase hydrogenation

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Supported gold catalysts are active catalysts for many reactions including hydrogenation. Although many studies aim to describe the catalytically active sites, there is disagreement about the nature of catalytically active sites in heterogeneous gold catalysis. In particular the oxidation state of the active gold species is still unclear. In hydrogenation cationic and reduced gold have been associated with high catalytic activity. However, there is a lack of in situ studies determining the oxidation state of gold under reaction conditions. We in situ studied the electronic properties of a supported gold catalyst (Au/CeO_2) in the high pressure liquid phase hydrogenation of nitrobenzene using HERFD XANES (high energy resolution fluorescence detection X-ray absorption near edge structure) spectroscopy [1]. Simultaneously, we monitored the conversion of nitrobenzene by ATR-FTIR (attenuated total reflectance-fourier transform) spectroscopy, which allowed a correlation of oxidation state and catalytic activity. To determine the influence of cationic and reduced Au species on the catalytic activity, as prepared Au/CeO_2 was subjected to different pretreatments to obtain catalysts with different fractions of Au^{3+} and Au^0. In the hydrogenation of nitrobenzene we observed that Au/CeO_2 that was free of measurable cationic gold was more active than Au/CeO_2 containing significant amounts of cationic gold. Further, remaining Au^{3+} reduced under reaction conditions without affecting the reaction rate. In conclusion, we found that the cationic gold that we detected did not contribute to high catalytic activity.

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Physical Chemistry **PC 13**

Amorphous Molybdenum Sulfide as Catalyst for Electrochemical Hydrogen Production in Water

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Amorphous molybdenum sulfide films are efficient hydrogen evolution catalysts in water. The films can be prepared via different electrochemical deposition methods. The method using consecutive cyclic voltammetry instead of a constant potential leads to the film with the highest and most stable catalytic activity. The film catalyzes proton reduction in a wide range of pHs and rather high geometric current densities are achieved at low overpotentials, e.g. up to 15 mA/cm^2 at η = 200 mV in 1 M H_2SO_4. The current efficiency for hydrogen production is quantitative. The molybdenum sulfide film can be doped with first-row transition metals by adding the respective metal ions to the deposition solution. The doped films show increased catalytic activity in terms of both, exchange current density and current densities at higher overpotentials.

Physical Chemistry **PC 14**

Photophysics of Tetrathiafulvalene and its Radical Cation

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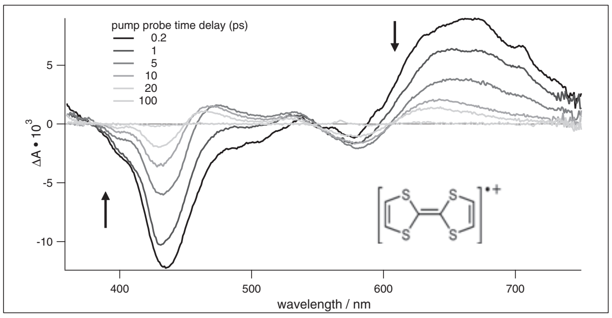
The great versatility and outstanding redox properties and stability of tetrathiafulvalene (TTF) make it one of the most studied molecules with more than thousand papers published each year concerning derivatives of TTF.[1] Despite its wide use in, e.g., highly sophisticated structures for artificial photosynthetic centres or fundamental research on electron transfer, the photophysics of TTF itself are still a subject of debate.[2] We provide a complete picture of the photophysics of TTF in its neutral and oxidised state. As will be shown, the behaviour is very distinct between the different oxidation states.[3]



Room temperature transient absorption spectra of TTF$^{\bullet+}$.

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Physical Chemistry **PC 15**

Infrared Multiple Photon Dissociation (IRMPD) Spectroscopy of Oxazine Dyes

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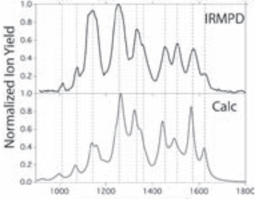
Oxazine dyes are used throughout the sciences for a variety of purposes, such as photo-stable laser dyes[1], histological stains for tumors[2] and fluorescent probes for light-harvesting nanoparticles[3]. The structure and energetic properties of Nile blue A, Cresyl violet, Brilliant cresyl blue and protonated Nile red have been probed using a combination of IRMPD spectroscopy, quantum chemical calculations and photodissociation experiments. A comparison of calculated and experimentally measured IRMPD spectra allows for structural elucidation and, for instance, can identify the site of protonation on Nile red, which significantly affects the photophysical properties. A comparison between the IRMPD spectra of all dyes shows many important differences which can be attributed to structural variances.



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Physical Chemistry **PC 16**

Two Dimensional Infrared Spectroscopy of Ice Ih

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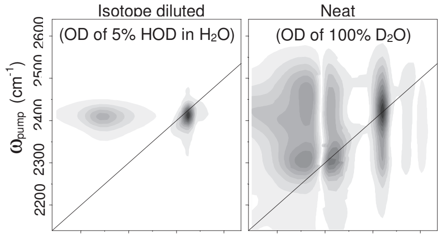
Proton disorder is an intriguing characteristic of many ice forms, due to its possible implication to vibrational exciton dynamics of the hydrogen bonded crystals [1]. With 2D IR spectroscopy of the OD stretch we address the aforementioned problem experimentally, investigating isotope diluted and neat ice Ih. For the isotope diluted case the main spectral features observed are the extremely broad 1-2 excited state transition, much broader than the corresponding 0-1 transition, in agreement with previous studies [2], as well as the presence of quantum beats. Complementary simulations in the framework of the Lippincott-Schroeder model qualitatively reproduce our experimental observations. Analysis of the neat ice 2D spectra reveals a truly exotic lineshape with a large distribution of beating frequencies. We conclude that these features reflect the complex interplay of vibrational excitons with Fermi resonances.



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Physical Chemistry **PC 17**

A miniaturized velocity filter for cold neutral molecules production

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The study of low-temperature chemical dynamics requires the production of intense beams of translationally and internally cold molecules. Such control over molecular degrees of freedom is especially challenging in the case of neutral species, and innovative experimental techniques need to be developed. One of the methods that has been successfully applied [1], consists in the filtering of polar molecules with an electrostatic guide [2,3].

We propose a new approach to this technique, based on the miniaturization of the guide and the use of stronger electric field gradients. Furthermore, the curved filter will be combined with several straight segments that can be switched on and off independently. An appropriate choice of the switching times will result in a band-pass filter with a tunable transmitted velocity up to ~500 m/s and a very low velocity spread.

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Physical Chemistry **PC 18**

A Thiophene-Based Anchoring Ligand and Its Heteroleptic Ru(II)-Complex for Efficient Thin-Film Dye-Sensitized Solar Cells

Nuttapol Pootrakulchote[1], Amaresh Mishra[2], Mingkui Wang[1], Soo-Jin Moon[1], Shaik M. Zakeeruddin[1], Michael Grätzel[1], and Peter Bäuerle[2]

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A novel heteroleptic Ru(II) complex (**BTC-2**) employing **5**,5′-(2,2′-bipyridine-4,4′-diyl)-*bis* (thiophene-2-carboxylic acid) (BTC) as the anchoring group and 4,4′-dinonyl-2,2′-bipiridyl and two thiocyanates as ligands is prepared. The photovoltaic performance and device stability achieved with this sensitizer are compared to those of the **Z-907** dye, which lacks the thiophene moieties. For thin mesoporous TiO_2 films, the devices with **BTC-2** achieve higher power conversion efficiencies than those of **Z-907**. Using a volatile electrolyte and a double layer 7+5 μm mesoporous TiO_2 film, **BTC-2** achieves a solar-to-electricity conversion efficiency of 9.1% under standard global AM 1.5 sunlight. Using this sensitizer in combination with a low volatile electrolyte, a photovoltaic efficiency of 8.3% is obtained under standard global AM 1.5 sunlight. These devices show excellent stability when subjected to light soaking at 60°C for 1000 h. Electrochemical impedance spectroscopy and transient photovoltage decay measurements are performed to help understand the changes in the photovoltaic parameters during the aging process. In solid state dye-sensitized solar cells (DSSCs) using an organic hole-transporting material (spiro-MeOTAD, 2,2′,7,7′-tetrakis-(*N*,*N*-di-*p*-methoxyphenyl-amine)-9,9′-spirobifluorene), the **BTC-2** sensitizer exhibits an overall power conversion efficiency of 3.6 % under AM 1.5 solar (100 mW c m^{-2}) irradiation.

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Physical Chemistry **PC 19**

Ultrafast spectroscopy of artificial self-organizing photosystems

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The development of smart artificial photosystems is an issue of increasing importance. The photophysical and electrochemical properties of these NDI systems can be tuned by varying the substituents on the NDI core (Figure A). Moreover, NDIs covalently attached to p-octiphenyl and oligophenylethynyl scaffolds can be self-organized as zipper assembly on a gold surface (Figure B), thereby providing materials with a spatially ordered and oriented redox gradient (1).

Using femtosecond techniques, we evidenced the population of a charge-separated state upon excitation of NDIs systems. The photophysical processes occurring in these systems, going from the "building blocks" – monomeric NDI – to highly organized architectures, will be discussed in detail.

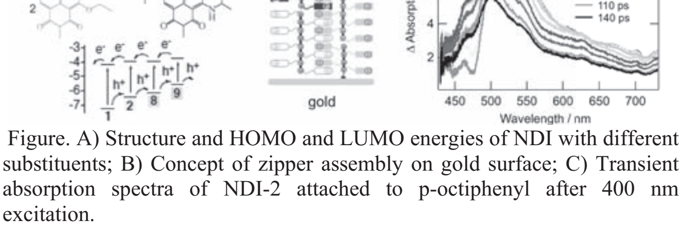

Figure. A) Structure and HOMO and LUMO energies of NDI with different substituents; B) Concept of zipper assembly on gold surface; C) Transient absorption spectra of NDI-2 attached to p-octiphenyl after 400 nm excitation.

Physical Chemistry **PC 20**

Human lens UV-filters: the diversity of the ultrafast deactivation mechanisms of the excited states

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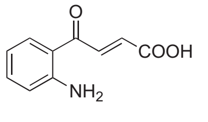
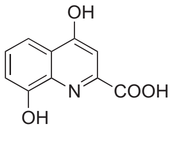
The lens of the human eye absorbs light in the 300-400 nm region due to the presence of low weight photochemically stable molecules – kynurenine (KN) and its derivatives. Recently we have studied the photophysics of KN – the parent compound for the whole family of lens UV filters. It has been shown that intermolecular hydrogen bonds play a crucial role in the ultrafast deactivation of KN excited states [1].

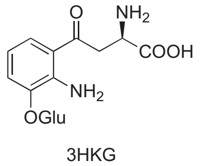
Here we present a femtosecond time-resolved optical spectroscopy study of the photophysics of three KN derivatives: (i) carboxyketoalkene (CKA), (ii) xanturenic acid (XAN) and (iii) 3-hydroxykynurenine glucoside (3HKG). Each of the studied compounds exhibits its own mechanism of ultrafast excited state decay based on: (i) inter/intra-molecular proton transfer, (ii) tautomeric transformations and (iii) intramolecular hydrogen bonding interactions.



CKA



XAN



3HKG

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Physical Chemistry **PC 21**

Pulse Trains with Unusual Angles in NMR

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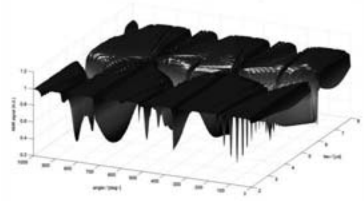
A standard method to measure transverse relaxation T_2 in Nuclear Magnetic Resonance (NMR) is the Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence [1,2]. After a 90° excitation pulse, a train of 180° pulses refocus the chemical shift while the spins relax with an exponential decay. In the presence of homonuclear J-couplings the decay is modulated and makes the determination of T_2 challenging. By decreasing the amplitude of the 180° pulses, the modulations can be quenched [3,4].

We changed the 180° pulses into other angles and observed the effects on the modulation of the decay. This showed interesting conditions with various unusual pulse angles. The experimental observations were confirmed by simulations based on the Liouville-von Neumann equation.



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Physical Chemistry **PC 22**

Excitation wavelength dependence of solvation dynamics in polar solvents

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Understanding the time-dependence of solvation is of uppermost importance as it is a key process for reactions in liquid solution; the dynamics of reactions such as electron or proton transfer may be controlled by the relaxation of the surrounding medium. Often, the physical properties of the medium are not sufficient to describe its behaviour and the effects it may have on a solute. Studying the solvation dynamics allows filling this void by examining the behaviour of the medium itself.

Due to its importance, solvation dynamics has been the subject of extensive studies over the past fifty years, but very few have investigated its excitation wavelength dependence and, if so, only in constrained media [1,2]. Therefore, we decided to investigate the solvation dynamics of a polar fluorescent probe in conventional polar solvents such as acetonitrile and dimethyl sulfoxide at room temperature by dynamic Stokes shift measurements [3] through fluorescence upconversion. Tuning the excitation wavelength, which could be considered as a way to select different subpopulations of the system, results in changes in solvation dynamics. It can be thought that each subpopulation has a particular solvation shell which would behave differently. This new insight into solvation dynamics in polar solvents at room temperature contributes to achieving a more complete picture of electron and proton transfer reactions in liquid solution, which are key reactions in chemistry and biology.

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Physical Chemistry **PC 23**

Photo-induced symmetry-breaking charge separation

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Photoinduced symmetry breaking (SB) charge separation (CS) occurs when a chromophore is surrounded by two (or more) identical electron donors or acceptors, but it can also happen between two identical molecular units. SB CS is one of the key steps of photosynthesis. Although the photosynthetic reaction center (RC) shows remarkable symmetry with the pigments arranged in two branches, electron transfer occurs only along the so called active branch. This preferential direction of CS has been ascribed to the asymmetry brought about by the protein environment[1, 2].

In order to find out whether photoexcitation can be at the origin of SB we have studied a bridged perylene-perylene system (Pe-B-Pe). Clear evidence of SB CS between two Pe units was obtained from transient absorption measurements (TA), which exhibit the parallel built up of Pe cation and anion bands. Using polarization sensitive TA we have been able to determine the direction of the charge flow. We found that both directions, i.e. from and towards the excited Pe unit, are operative and that their associated rate constants differ by less than a factor 2.

Two-dimensional (2D) electronic spectroscopy permits more detailed insight into the interactions and dynamics of multichromophre systems. We will present 2D electronic spectra of Pe-B-Pe obtained from heterodyne-detected photon echo measurements. Moreover, we will discuss the reason for the absence of a preferred CS direction in Pe-B-Pe and the conditions where a preferred direction could possibly be observed.

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Physical Chemistry **PC 24**

Free Energy Dependence of Back Electron Transfer in Pure Donating Solvents

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[2]Institute of Physical Chemistry, Polish Academy of Science, Warsaw

Electron transfer (ET) constitutes the simplest and at the same time most elementary “chemical” reaction rendering it a benchmark for the understanding of basically every other chemical reaction.

Here we present a case study on the free energy dependence of ET in a pure reactive solvent. Charge separation in such media proceeds essentially without the need of (translational) diffusion and has been the subject of various extensive studies.[2] However, the subsequent charge recombination process has not received comparable attention. In fact, the few existing studies did not vary the driving force in a systematic way or attempted to span a sufficiently large energetic diapason necessary for the observation of clear-cut trends.[3]

We apply femtosecond time resolved optical spectroscopy (fluorescence and absorption) to a set of fluorophores in an aromatic amine, covering the broad driving force range of 1.5eV. We are confident that by doing so and comparing the obtained kinetics with those obtained in inert solvents of similar viscosity will allow for a deeper understanding of the underlying ET reaction in this particular case. Such kinetics are expected to be simpler with respect to those in the latter case due to a much narrower initial distribution of ions in the reacting solvent.

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Physical Chemistry **PC 25**

Ultrafast electronic and vibrational relaxation in free base and metallo-porphyrins

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Metalloporphyrins are at the center of an intensive research activity aimed at designing functional and scalable artificial photosystems. This necessitates the understanding of their photocycle, which is the aim of our work.
With our sub-100 fs resolution fluorescence set-up with broadband detection, we carried out studies on metalloporphyrins with partially filled metal 3d shells and compared them with Zn- and free base porphyrins. We observed that the energy structure of the empty states of the central atom speeds up all dynamical processes by almost two orders of magnitude. For Zn- and free base porphyrins, we determined their photocycle in a more complete way than previously reported. [1, 2] Moreover, in free base porphyrins we observed pulse-limited internal conversion followed by vibrational coherences in both the tetraphenyl- and octaethyl-porphyrin (TPP and OEP) analogues.

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Physical Chemistry **PC 27**

Spin switching dynamics in the 2D coordination network $[Zn_{1-x}Fe_x(bbtr)_3]A_2$ ($A = ClO_4^-, BF_4^-$): role of elastic interactions

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In the 2D network of the dilute system $[Zn_{1-x}Fe_x(bbtr)_3](ClO_4)_2$ ($x = 0.02$, bbtr = 1,4-di(1,2,3-triazol-1-yl)butane), the iron(II) centres stay essentially in the high-spin (HS) state down to l0 K. For increasing values of x the low-spin (LS) fraction at 10 K increases. Already at $x = 0.38$, a crystallographic phase transition is triggered by the spin transition. We have studied the HS⇔LS relaxation dynamics over a wide temperature range using wavelength selective excitation. The LS→HS relaxation rate constant increases by 14 orders of magnitude, that is, from $5x10^{-7}$ s^{-1} (τ = 25 days) at 40 K to $3x10^{7}$ s^{-1} (τ = 30 ns) at 220 K for $x = 0.02$ [1]. The neat BF_4^- analogue stays in the HS down to 10 K, but it can be converted to the LS state via reverse LIESST, and it shows true light induced bistability below 100K. The variation of elastic interactions through LIESST, reverse LIESST and the LS⇔HS relaxation dynamics of $[Zn_{1-x}Fe_x(bbtr)_3](ClO_4)_2$ mixed crystal as well as the BF_4^- derivative could thus help to design highly cooperative systems for efficient optical switching and memory devices.

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Physical Chemistry **PC 26**

Broadband ^{13}C Homodecoupling for Fully-Enriched Compounds

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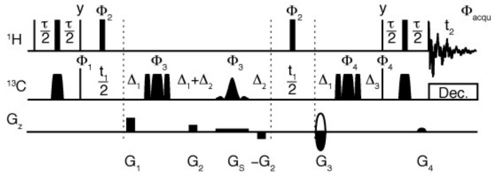
Removing homonuclear ^{13}C scalar couplings is a challenging NMR issue when ^{13}C-fully labeled compounds are studied by NMR methods. The solutions reported so far for suppressing ^{13}C multiplet splittings in the indirect dimension have mainly focused on protein NMR experiments where band-selective decoupling was successfully implemented. However, the existing methods are not applicable when ^{13}C resonances are spread over a wide spectral range. We introduced a broadband ^{13}C-homodecoupled HSQC experiment (BBHD-HSQC) [1] which effectively eliminates ^{13}C-^{13}C couplings in the indirect ^{13}C dimension. It is based on a spatial encoding of chemical shift interactions relying on a Zanger-Sterk element [2] suitably implemented in the 2D pulse sequence. The performances of BBHD-HSQC are illustrated on fully labeled cholesterol, produced by a modified yeast strain [3].



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Physical Chemistry **PC 28**

Mono- and bimetallic Rh and Pt: Influence of the noble metal position on Sulfur poisoning of NO_x storage reduction catalysts

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To decrease automobile emission of lean combustion engines, NO_x storage-reduction (NSR) catalysts were developed. These catalysts trap NO_x under fuel lean conditions as metal-nitrates, which are subsequently reduced under rich conditions. Mono- and bimetallic Rh and Pt based NO_x storage-reduction (NSR) catalysts with noble metals deposited on the Al_2O_3 or $BaCO_3$ component were prepared by means of flame spray pyrolysis using a two nozzle system [1], as shown in Fig. 1. NSR performance was investigated in the absence and presence of SO_2 (25 ppm). Superior performance was observed for catalysts with noble metals located on $BaCO_3$. Rh-containing catalysts showed higher SO_2 tolerance making them interesting for technical applications.

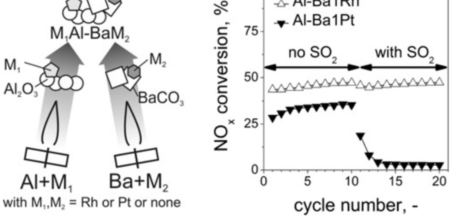

Fig. 1: Synthesis of Rh and Pt catalysts with controlled metal deposition and their NO_x conversion performance in absence and presence of 25 ppm SO_2.

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Physical Chemistry **PC 29**

Ultrafast Bulk Dynamics of the Potential Interfacial Probe Methyl Orange

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Interfaces between aqueous and hydrophobic phases are encountered in every biological system, demonstrating their aboundance and importance. There is thus a stringent need to increase the knowledge about these interfaces, which, up to now, is still poor.

As the information about interfacial properties cannot easily be accessed by standard bulk techniques, one powerful option is to take recourse to second-order non-linear spectroscopy, like for example second harmonic generation (SHG), which has proven a valuable tool for this purpose during the last decades [1,2].

The long-term aim of our studies is to explore the properties of interfaces by investigating the excited-state dynamics of interfacial probes at liquid-liquid interfaces using the femtosecond time-resolved SHG technique, which is readily available in our lab [3]. Due to its structure, the azo-dye methyl orange was considered a suitable candidate for these studies. In order to be able to draw conclusions about the properties of the investigated interface from the dynamic behavior of the probe molecule at the interface, it is essential that the bulk behavior of the molecule is well known. In the case of methyl orange only very little information about the excited state photophysics can be found in the literature.

In this study we thus present the ultrafast excited-state bulk dynamics of methyl orange in water and water-glycerol mixtures studied by femtosecond transient absorption and fluorescence up-conversion, as needed for comparison with the observations made at the interface.

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Physical Chemistry **PC 30**

Influence of $A(B,Pd)O_{3\pm\delta}$ (A= La, Y; B= Mn, Fe, Co) composition on the state of Pd

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Palladium-based perovskite-type oxides are potential materials for automotive applications and can be regarded as catalyst precursors. The ease of formation of a solid solution between Pd and ABO_3 allows designing catalysts with peculiar catalytic properties and reducing the precious metal loadings. However, occupation of the B-site by Pd is also dependent from the ABO_3 formulation. $La(B,Pd)O_3$ (B= Co, Fe, Mn) perovskite type oxides and $Y(Fe,Pd)O_3$ were prepared by the amorphous citrate method [1] and characterized with respect to the state of Pd using XAS, XPS, H_2-TPR, and in-situ XANES H_2-TPR. Incorporation of Pd in the ABO_3 structure was achieved for $LaFeO_3$ and $LaCoO_3$, Pd exhibiting the typical XANES signature of Pd^{n+} (n>2) in octahedral coordination. Contrarily, $LaMnO_3$ and $YFeO_3$ showing XANES features and reduction behavior typical of segregated PdO at the catalyst surface [2]. The different Pd states strongly influenced catalytic activity for CH_4 combustion between 200-900°C. Highest catalytic activity was found for $La(Mn,Pd)O_3$ and $Y(Fe,Pd)O_3$, as Pd was accessible to CH_4. Consequently, lowest catalytic activity was observed for $La(Fe,Pd)O_3$ and $La(Co,Pd)O_3$. The different trend of Pd to occupy the B-site is discussed on the base of the possible coordination environments that Pd can adopt and on ionic radii considerations.

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Physical Chemistry **PC 31**

Organisation of organic donor-acceptor blends into 2D-photonic crystals for enhanced light absorption

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We propose a quick and cheap method to manufacture an organic semiconducting 2D-photonic crystal. Such structures enhance the light-matter interaction through "slow Bloch modes" in the material and are thus promising candidates for the improvement of light harvesting in organic photovoltaic devices [1]. Micro-contact printing [2] was used to induce order in self-assembled thin films of small organic semiconducting molecules. Solutions of a cyanine dye and a fullerene derivative (PCBM) -used as active layer in organic photovoltaic devices- were spin cast and underwent lateral phase separation and hierarchical structuring [3] on a patterned self-assembled film surface. Macroscopic ordered samples with a wide periodicity range (0.5 to 5 µm) could be manufactured. Atomic force microscopy (AFM) showed a large variety of structured morphologies. By adjusting the system's natural decomposition wavelength and the characteristic dimensions of the surface pattern, the phase separation contrast is highest. Optical measurement on transparent patterned substrates also showed the presence of so-called H-aggregates which exhibit interesting optical properties. Such organization of the photoactive layer at micrometer scale is suitable for improved light harvesting in photovoltaic devices through scattering, interference or in coupling of "slow Bloch modes".

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Physical Chemistry **PC 32**

High-resolution photoelectron spectroscopic investigation of propene and its isotopomers

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The pulsed-field-ionisation zero-kinetic-energy (PFI-ZEKE) photoelectron spectra of CH_3CHCH_2 (propene), CD_3CDCD_2 and several partially deuterated isotopomers have been recorded in the region of their adiabatic ionisation thresholds. The spectra consist of many vibrational bands, some of which partially rotationally resolved [1], associated with the low-frequency modes. The analysis of the complex vibrational structure could only be achieved by observing the frequency shifts upon deuteration of selected sites of the propene molecule and has led to new assignments of the vibrational bands at low energy and thus answers to questions raised by earlier studies [2]. Two anharmonic progressions have been identified and assigned to the two torsional motions of the propene cation, namely the methyl internal rotation and the CH_2 twist. The intensity distributions in these spectra provide information on the vibronic coupling in the molecular cations. Vibronic interactions are revealed by unexpected vibrational intensity distributions [2], perturbations of the rotational intensity distributions [1], and pronounced changes of the spectral features resulting from isotopic substitutions.

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Physical Chemistry **PC 33**

Amino Acid Peroxyl Radicals: Reaction with Urate

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Proteins are significant targets for partly reduced oxygen species *in vivo*. This results in random formation of radicals on the amino acid residues (AA$^\bullet$) of the protein, which in turn, in the presence of oxygen, can yield the corresponding peroxyl radicals (AAOO$^\bullet$). Both radical types can cause further biological damage. Urate, an important antioxidant, is able to repair tyrosine and tryptophan radicals in various proteins *in vitro*.[1,2]

We studied the *N*-acetylamide derivatives of glycine, alanine and proline and generated the amino acid peroxyl radicals by pulse radiolysis.

The peroxyl radicals of the amino acids studied were reduced by oxidizing urate to the urate radical. The reaction was followed at 340 nm, where urate radical absorbs, and a yield of formation of 30% was calculated. Surprisingly, the urate radical formation is not dependent on the urate concentration and the derived rate constants are all close to 10^3 s^{-1}. This suggests initial formation of an adduct between AAOO$^\bullet$ and urate, which then further decays to form urate radicals. It is to be stressed that reaction of AAOO$^\bullet$ and urate gives rise to hydroperoxides (AAOOH) that are also reactive molecules. Possibly urate could “repair” protein radicals (AA$^\bullet$) and protect from biological damage *in vivo*, given its high concentration in living organisms.

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Physical Chemistry **PC 34**

The structure of high-n Rydberg states of molecular hydrogen

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High-resolution spectroscopic investigations of molecular Rydberg states at different values of the principal quantum number n enable one to study the interaction between the Rydberg electron and the molecular ion core. With increasing n values, the electron motion gradually decouples from the motion of the molecular ion core. The decoupling is accompanied by very characteristic perturbations of the spectral patterns and by spin-rovibronic channel interactions which provide extremely detailed information on the electron-ion system.

We present the results of a combined experimental and theoretical study of the s, p, d, and f Rydberg states of molecular hydrogen. Experimentally, high-resolution laser and millimeter-wave spectra of Rydberg states with principal quantum numbers between 30 and 60 have been recorded with a precision of better than 100 kHz (3×10^{-6} cm^{-1}). Theoretically, multichannel quantum defect theory has been employed to analyze the spectra: first, eigenquantum defect functions were determined *ab initio* in R-matrix calculations; second, the eigenquantum defect functions were refined until agreement with the experimental data was reached. The investigation allows to extract the electron binding energy of the high-n Rydberg states as well as the hyperfine structure and the energies of rotationally excited states of H_2^+ with an accuracy on the order of 100 kHz.

Physical Chemistry **PC 35**

Luminescence studies of rare earth doped $Sr_4Al_{14}O_{25}$

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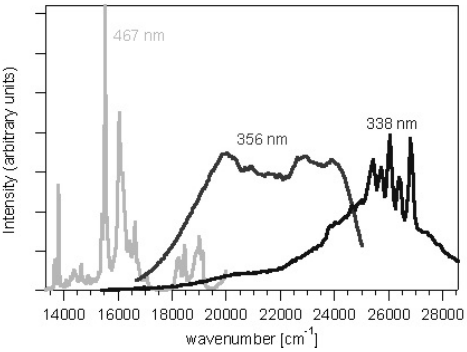
Rare earth ions in crystals have useful optical properties. Strontium aluminates, codoped with Eu^{2+} and Dy^{3+} are persistent phosphors with decay times of hours. In this work, we address potential excitation transfer processes between Eu^{2+} and other rare earth ions. Experiments on samples (prepared by B. Walfort, Tritec AG, Teufen) codoped with Eu^{2+} and Pr^{3+} suggest the possibility of energy transfer from Eu^{2+} to Pr^{3+}. As can be seen in the figure below, excitation at 338 nm (29580 cm^{-1}, corresponding to the energy difference between the excited $^1D_2$ and $^1S_0$ levels) leads to sharp emission bands tentatively assigned to emission bands from the $^1S_0$ to the $^1I_6$ and ^3P_J levels. The population of the $^1D_2$ level is achieved through the f-d absorption of the Eu^{2+} ion.



Emission spectra at 60K excited with 338, 356 and 467 nm.

Physical Chemistry **PC 36**

Synthesis and characterization of new borohydrides

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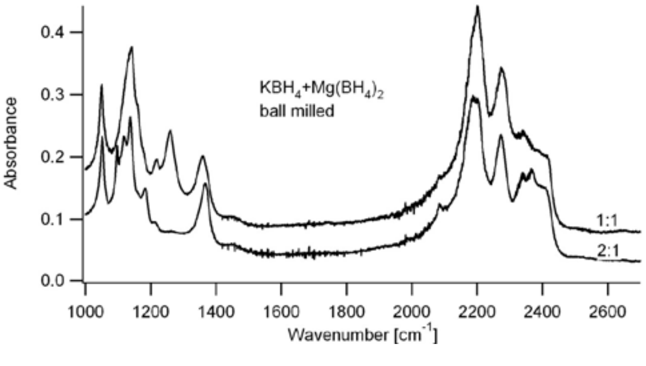
Metal borohydrides are interesting materials for hydrogen storage, due their large gravimetric and volumetric hydrogen content.

Different synthetic methods to prepare $Sr(BH_4)_2$, in solution as well as ball milled, are presented. Further, new bimetallic borohydrides such as $K_2Mg(BH_4)_4$ are synthesized and characterized.

The structural data obtained from X-ray powder diffraction is compared with the results of periodic-DFT calculations.

IR spectroscopy was used to study the prepared sample and to monitor the removal of solvent under high vacuum.



Physical Chemistry **PC 37**

Temperature dependence of the transition interference between f-f and f-d transitions of Sm^{2+} in matlockite hosts

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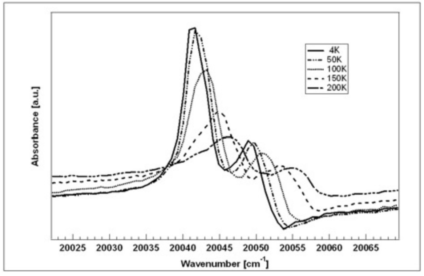
The interaction between discrete electronic levels and an overlapping continuum can give rise to interference effects producing characteristically asymmetric line shapes of the transition to the discrete levels which is referred as Fano resonance [1]. The Fano resonance were observed between f-f and f-d transitions in single crystals of SrFCl doped with Sm^{2+} [2]. In matlockite host crystals (MFX where M=Ba, Sr and X=Br, Cl) the observed $^7F_0$ $(A_1) \rightarrow {}^5D_3$ (E) transitions of the Sm^{2+} ion were anomalously strong and exhibit at 4K a pronounced Fano double line profile which broadens and shifts to the higher energy with temperature but persists up to RT. The Fano resonances were also observed in Sm^{2+} in all MFX hosts at higher energy around 24000 cm^{-1} originating from higher ^5L_J states. The figure showed the absorption resonance of Sm^{2+} in SrFBr originating from $^7F_0$ $(A_1) \rightarrow {}^5D_3$ (E) transitions at different temperatures.



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Physical Chemistry **PC 38**

Conformational Dynamics and Diversity of Single G Protein-Coupled Receptors Trapped in Solution or Tracked in Living Cells

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Single-molecule spectroscopy has proven to be among the most suited techniques to address biological questions as it can probe the inherent molecular heterogeneity of biological systems by removing ensemble averaging or lead to drastic improvements in spatial resolution. We show herein how in particular trapping, tracking or localization of individual fluorescent molecules can advance our understanding of the molecular mechanisms underlying activation of G protein-coupled receptors (GPCRs), a vast family of transmembrane proteins which are crucial drug targets.

We focus on our use of an Anti-Brownian ELectrokinetic (ABEL) trap, a novel device which allows individual nanoscale fluorescent objects to be studied in solution without requiring chemical immobilization, to investigate the conformational dynamics of the β_2-adrenergic receptor (β_2AR) in the presence and in the absence of an agonist. By using a conformation-sensitive reporter dye, we observe a diversity of fluorescence intensity and lifetime levels in individual β_2AR molecules, indicating changes in radiative lifetime and the existence of a vast range of discrete conformational states. We find that agonist binding increases the dwell times of these states and monitor millisecond fluctuations within these states.

We further describe our current efforts to use single-particle tracking and localization microscopy techniques in live and fixed cells in order to understand the mechanisms by which engineered ligands inhibit CCR5, another GPCR which is the major HIV co-receptor and which can be efficiently targeted to prevent HIV infection.

Physical Chemistry **PC 39**

Conformation-selective investigation of peptide fragment ions by cold ion photofragment spectroscopy

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Collision-induced dissociation (CID), coupled to tandem mass spectrometry (MS/MS) or MS^n, is a versatile tool for the determination of the sequences of peptides and proteins. The breakage of amide bonds can lead to sequence-informative *b* or *y* ions, in which the charge resides on the *N*- or *C*-terminal fragment, respectively.[1] However, information on the sequence can be lost by permutation, e.g. via macro-cyclization.[2] Structural investigation of the intermediates in peptide fragmentation is crucial to elucidate the mechanisms and assess conditions that can lead to sequence scrambling.

We perform conformer-selective spectroscopic investigations of peptide fragment ions in a 22-pole ion trap at 4 K.[3] The UV spectra of mass-selected b_4 and a_4 fragment ions of Leucine-enkephalin (YGGFL) are acquired by photofragmentation spectroscopy. IR spectra can be selectively measured by a powerful double-resonance IR depletion technique. The number of contributing isomers can thus be assessed in a straightforward way. The high-resolution spectra, which are further supported by isotopic substitution, constitute an important benchmark for theoretical DFT calculations.

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Physical Chemistry **PC 40**

Microreactor: mixing and precipitation

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Precipitation in microreactors presents an attractive route for the production of small particles. As mixing in microreactors is very fast, high levels of supersaturation can be created which leads to fast nucleation and, ideally, to small particles. However, processing of solids in microreactors is challenging as deposition and clogging can occur. In this work, a commercial mixer (Ehrfeld 0111, Ehrfeld BTS, Germany) whose design includes a spring valve is investigated for its mixing performance. The valve requires the lower volumetric flow to be high enough to overcome resistance of the valve spring. The other stream has to be set equal or higher so that no backmixing occurs. The mixing is evaluated using a reaction system consisting of the fast neutralization of sodiumhydroxid (1) and the slow hydrolisis of 2,2-dimethylpropene (DMP) (2).

$$H^+ + OH^- = H_2O \qquad (1)$$

$$H^+ + CH_3C(OCH_3)_2CH_3 + H_2O = H^+ + CH_3COCH_3 + 2CH_3OH \qquad (2)$$

For fast mixing only (1) takes place whereas for slow mixing also DMP (2) can be converted. Formation of methanol is thus selected to quantify mixing. Our data is compared with literature data for two types of jet mixers [1] and a V-type mixer [2,3]. For a given flow rate the jet mixers give the best mixing whereas the valve mixer lies in between the jet and the V-type mixer. The work presents a first step in the evaluation of commercial microreactors for processing solids.

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Physical Chemistry **PC 41**

“Brick and Mortar” Nanostructured TiO_2 Electrodes for Application in Dye-Sensitized Solar Cells with Ionic-Liquid Electrolytes

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The introduction of ionic liquids into electrolyte systems for dye-sensitized solar cells (DSCs) has been shown to produce devices with excellent levels of both performance and long-term stability [1]. The relatively high viscosity of these electrolytes, however, is still a limiting factor for the overall efficiency, and manifests itself in mass transport problems affecting mostly the photocurrent under full sunlight. In order to facilitate the diffusion through the mesoporous TiO_2 layer, new structures with larger pores need to be fabricated. Recently, we reported a “brick and mortar” strategy for the fabrication of TiO_2 layers by using a combination of nanocrystalline and sol-gel precursors in a surfactant-templated self-assembly process. As-produced electrodes have been successfully implemented in DSCs employing liquid and non-volatile electrolytes [2]. Here we present DSCs based on solvent-free ionic-liquid electrolytes and tailor-made TiO_2 layers. Transparent and thin (2 μm) “brick and mortar” layers in combination with a novel organic sensitizer (Y123) and an ionic liquid electrolyte resulted in efficiencies of over 6 % with short-circuit current densities higher than 11 mA/cm^2. The device analysis includes typical I-V measurements, photocurrent and photovoltage transient analysis, and electrochemical impedance spectroscopy.

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Physical Chemistry **PC 43**

Photoinduced Translational Dynamics of Doped Helium Nanodroplets

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The photoinduced translational dynamics of species solvated in helium nanodroplets has been investigated with a variety of spectroscopic techniques. It has been found that for some solutes the interaction with the helium environment changes upon electronic excitations from attractive to repulsive. As a result, the excited species are ejected from the droplets. Using ion imaging techniques, the speed distributions of the ejected atoms or molecules have been determined. The relation of these speed distributions to the critical Landau velocity, the velocity below which no energy and momentum can be transferred from a moving object to the superfluid helium environment, will be discussed.

Physical Chemistry **PC 42**

Exciton splitting in molecular dimers: The jet-cooled 2-ketoquinoline dimer

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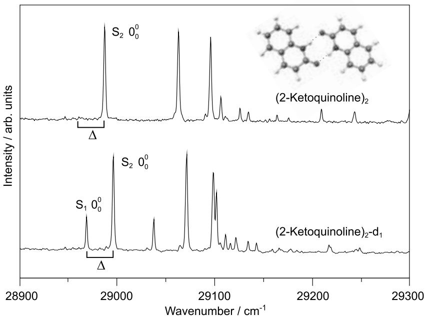
We have previously investigated the S_1/S_2 excitonic splitting Δ in the optical spectra of the supersonically cooled symmetric molecular homodimers (2-pyridone)$_2$ and (2-aminopyridine)$_2$ and their corresponding ^{13}C- and d$_1$-isotopomers [1],[2]. The experimental S_1/S_2 excitonic splittings are in good agreement with the quenched S_1/S_2 energy gaps resulting from the multimode vibronic coupling model [2] using high-level *ab initio* calculations. The quenching arises from the vibronic coupling to the optically active intramolecular vibrations [2]. We extend these results to the system (2-ketoquinoline)$_2$ and the (2KQ)$_2$-d$_1$ isotopomer and compare them to calculated exciton splittings.



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Physical Chemistry **PC 44**

Analysis of the vibrational structure of CH_3I and HC_2I in the ionic ground state

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The pulsed-field-ionization zero-kinetic-energy photoelectron spectra of the $\tilde{X}^{+}\,^{2}E_{3/2} \leftarrow \tilde{X}\,^{1}A_1$ transitions of iodomethane (CH_3I) and of the $X^{+}\,^{2}\Pi_{3/2} \leftarrow X\,^{1}\Sigma^{+}$ transitions of the iodoacetylene (HC_2I) have been recorded at high resolution using a narrow bandwidth vacuum ultraviolet (VUV) laser system [1] and optimized electric field pulse sequences [2]. CH_3I^+ and HC_2I^+ exhibit a strong spin-orbit coupling arising from the fact that after ionization from one of the p_{xy} lone pairs of I the electron hole is localized on the iodine atom [3].

Studies of the lowest electronic state of CH_3I^+ and HC_2I^+ by high-resolution photoelectron spectroscopy provide information on the complex interplay between spin-orbit interactions and vibronic interactions such as the Jahn-Teller and Renner-Teller effects.

Support by the Swiss National Science Foundation and the ETH Zürich is gratefully acknowledged.

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Physical Chemistry **PC 45**

Physical Chemistry

Preparation and active phase composition of Pd-substituted perovskite-type oxides as three-way-catalysts

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Natural gas and bio-gas are encountering growing public awareness as potential alternative fuels to gasoline and diesel. Pd-substituted perovskite materials receive increasing attention in the field of car exhaust after treatment of stoichiometric engines, due to their 'self-regeneration' property [1].

In this study, perovskite-type oxides (ABO_3, A=La, Y; B=Mn, Fe), containing Pd, were prepared using flame spray synthesis (FSS) and were characterized by XRD, H2-TPR, BET and IR. Their activity as three-way-catalysts (TWC) for the abatement of carbon monoxide, methane and nitrogen oxides, emitted from stoichiometrically operating natural-gas-fuelled vehicles, was investigated under simulated exhaust conditions in lab-scale reactor. A post synthesis treatment, i.e. in furnace or in oxygen, was needed for structure stabilization and crucial for the catalytic activity. The characterization data reveal that, despite the one-pot synthesis approach, Pd can be found in the form of segregated PdO particles and constitutes the active phase. Among the various samples, Y-based ones demonstrated the most active for methane oxidation, the temperature of 50% CH_4 conversion being 420 °C for $Y(Mn,Pd)O_3$.

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Physical Chemistry **PC 46**

Supersonic jet UV spectra of cytosine and 5-fluorocytosine

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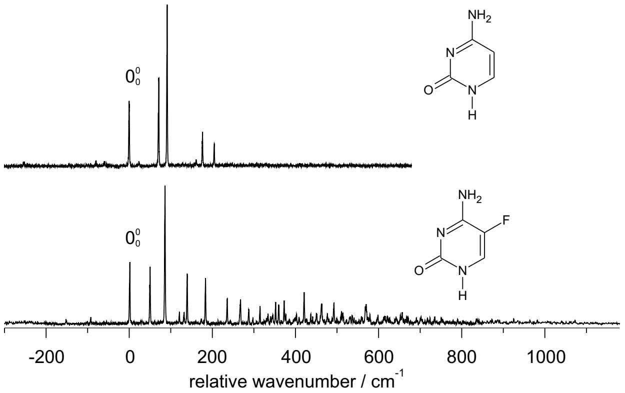
The two-color resonant two-photon ionization (2C-R2PI) spectrum of jet-cooled cytosine has been measured and exhibits five vibronic bands within 200 cm^{-1} [1]. The spectrum is assigned to the amino-oxo tautomer, the canonical form of cytosine present in DNA [1]. We have investigated the 2C-R2PI spectrum of 5-fluorocytosine (5FCyt) and compare it to the spectrum of cytosine. The vibronic bands of 5FCyt extend up to $\sim$800 cm^{-1} above the 0_0^0, much higher than for cytosine. This implies a higher excited-barrier for 5FCyt that hinders the access to an $S_1 \rightarrow S_0$ conical intersection.



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Physical Chemistry **PC 47**

Amplification of Linear Dichroism for Ultrasensitive Femtosecond IR Spectroscopy.

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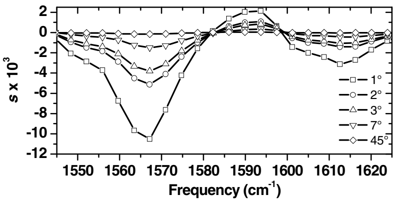
We demonstrate strong amplification of polarization-sensitive transient IR-signals using a pseudo-null crossed polarizer technique, where an intense IR probe is attenuated after sample with a polarizer at an angle 90+β with respect to its polarization, while the relative pump beam polarization is set to ±45°. We adapted the technique using photoelastic modulators, which allow us to measure amplified linear dichroism at kilohertz repetition rates. The method was applied to a photoswitch of the N-alkylated Schiff base family [1] in order to demonstrate its potential of strongly enhancing sensitivity and signal to noise in ultrafast transient IR experiments [2], to simplify spectra and to determine intramolecular transition dipole orientations (Fig.1.). Extension of the same measurement principle to 2D-IR and to higher order spectroscopies will also be discussed.



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Physical Chemistry **PC 48**

Ultrafast broadband fluorescence up-conversion of N-Acetyl-L-tryptophan amide (NATA)

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N-Acetyl-L-tryptophan amide (NATA) is a close analogue of the optically-active tryptophan amino acid residue in proteins. Equivalently to tryptophan, it can be regarded as a convenient fluorescent probe to investigate structural transformations and solvation effects in biological macromolecular systems.[1] In this respect, an advantage of NATA compared to tryptophan is the fact that it features a simpler single-lifetime (~3 ns) excited state decay. The photo-physics of tryptophan and its derivatives is rather complex and some issues are still not fully understood, such as the mechanisms leading to fluorescence quenching. Since quenching of NATA emission is found to be more effective in protic solvents, site-specific solvation associated to H-bonding could be a key step in the road leading to eventual fluorescence quenching.

Fluorescence up-conversion is a powerful experimental approach to investigate these matters, since it selectively provides a detailed picture of ultrafast excited state(s) relaxation, as we recently demonstrated for the case of tryptophan in water [2]. We report here broadband fluorescence upconversion studies of NATA in the UV spectral range. Experiments were carried out in solvents (MetOH, ACN and H_2O) differing in both their dielectric constant and in their H-bonding properties. Experimental data provide plentiful information on the solvation dynamics of the chromophore and on the extent to which H-bonding dynamics affects its excited-state properties.

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Physical Chemistry **PC 49**

Charge carrier dynamics of dye sensitized TiO_2 films studied by nanosecond diffuse reflectance spectroscopy

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The performance of a solar cell device depends on the kinetic competition between charge injection, electron back transfer and dye regeneration processes. To study these processes in a device, transient absorption spectroscopy is done on dye sensitized TiO_2 transparent films as a model system. The high efficiency devices usually consist of a scattering layer made of 400 nm TiO_2 particles on top of a high surface area mesoporous transparent film, that makes the film optically opaque [1,2]. Therefore devices based on photoanodes made of these films as photoactive layer and on other morphologies of TiO_2, like nanostructured fibers or anodized nanotubes films, cannot be studied by transient techniques in transmission mode.
we have developed nanosencond diffuse reflectance technique to study electron back transfer and dye regeneration process on a complete cell device. Samples are excited by pulses of a ns pulsed laser (520 nm, 5 ns duration). The probe light is provided by a Xe lamp and the diffuse reflectance of the sample was collected by an ellipsoidal mirror. The results show a faster recombination of injected electrons with the oxidized dye, in the the films of TiO_2 consisting of 400 nm particles versus transparent film made of 20 nm particles. The electron lifetime was measured as being less than 50 µs and more than 200 µs for opaque and transparent films, respectively.

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Physical Chemistry **PC 50**

Carrier dynamics in small molecule organic solar cells

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In the large domain of organic photovoltaics, small soluble molecules are gaining more and more interest. Compared to polymers, small molecules offer a large panel of advantages like ease of synthesis, monodisperse behavior as well as high purity [1]. Lately, 2% efficiency has been reported by Fan and coworkers for doped cyanine dyes as a donor material in bilayer heterojunction organic solar cells [2].

Two major issues for these soluble cyanine dyes are here reported.
First, the understanding of the role of cyanine aggregation in charge separation is addressed. Actually, Fan and coworkers speculate a long exciton diffusion length in cyanine/C60 heterojunction as a conclusive explanation for the unexpected large IPCE value in 30 nm thick cyanine films. However, it is still an open question whether the exciton diffuses along the aggregates or dissociates within the active layer [3]. A deep study of the ultrafast charge separation processes is therefore necessary.
Secondly, the anodic material has a large effect on the hole transfer kinetics from the cyanine donor. More efforts will be devoted in matching the HOMO energy levels of the cyanine donor and the anodic material.

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Physical Chemistry **PC 51**

Carrier dynamics in solid-state dye-sensitized solar cells studied with time-resolved spectroscopy

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Solid-state dye-sensitized solar cells (SSDSCs) emerge as a substantial alternative to overcome problems related to leakeage and corrosion in liquid electrolyte devices [1]. Nowadays, systems based on solid-state hole transport materials (HTM) reach 6% efficiency [2], while liquid DSCs account for 12%. In order to understand the origin of the limitations in solid-state systems, it is crucial to gain deeper insight into the study of carrier dynamics, namely the kinetics of holes and electrons following light excitation.

We wish to report on the effects of doping, pore filling and various other parameters on the hole injection kinetics as determined by femtosecond transient absorption studies. On the other hand, the slower processes of charge recombination in the microsecond to millisecond time regime were investigated by laser flash photolysis.

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Physical Chemistry **PC 52**

Spectra of Cold Molecular Ions from Hot Helium Nanodroplets

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The function of a molecule is intimately related to its structure. In the quest for a better understanding of molecular function, the development of spectroscopic methods to elucidate molecular structures increasingly takes central stage. The amount of detail that can be derived from spectra depends on the experimental conditions, most notably on the temperature of the sample and the intermolecular interactions a molecule experiences. Helium nanodroplets provide in this respect an almost ideal matrix[1, 2]. For neutral molecules, helium nanodroplet spectroscopy thus has led to important discoveries related to the structure of key molecular systems and has provided insight into the mechanisms underlying chemical reaction.

Compared to the level of sophistication that has been reached for neutrals, the spectroscopic exploration of ions is still in its infancy. The use of helium droplets as a cryogenic matrix could potentially solve many of the technical challenges associated with recording high-resolution spectra of cold molecular ions. Here, we will present a method to record spectra of ion containing helium nanodroplets that finds its roots in the nonthermal cooling dynamics of excited molecular ions. The influence of the helium environment on these spectra will also be discussed.

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Physical Chemistry **PC 53**

Supersonic Jet Spectroscopy of the Adenine Analogues 9-Methyl- and 7-Methyl-2-Aminopurine

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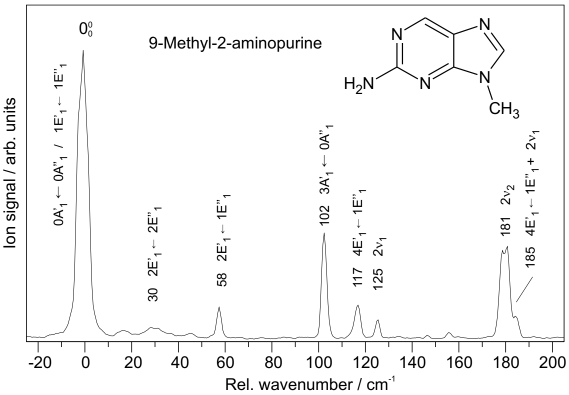
Recently, we have investigated the UV vibronic spectra and excited-state nonradiative processes of supersonic jet-cooled 9H-2-aminopurine and its water clusters by two-color resonant two-photon ionization spectroscopy [1, 2]. Here, we extend the study of adenine analogues to 9-methyl- and 7-methyl-2-aminopurine (9M2AP and 7M2AP). The vibronic spectra of 9M2AP and 7M2AP show methyl torsional subbands, from which we extract S_0 and S_1 ($^1\pi\pi^*$) state torsional barriers. For 9M2AP we find a ~100 ps S_1 state lifetime and rapid intersystem crossing to the T_1 ($^3\pi\pi^*$) state similar to 9H-2-aminopurine.



[1] S. Lobsiger, R. K. Sinha, M. Trachsel, S. Leutwyler *J. Chem. Phys.*, **2011**, *134*, 114307.

[2] R. K. Sinha, S. Lobsiger, M. Trachsel, S. Leutwyler *J. Phys. Chem. A*, **2011**, *published online, DOI:10.1021/jp111469n.*

Physical Chemistry **PC 54**

S_0 and S_1 state geometry and methyl torsional barriers of 5-methyl-2-hydroxypyrimidine

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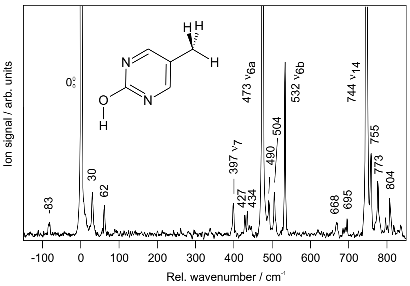
We have investigated the two-color resonant two-photon ionization spectrum of jet-cooled 5-methyl-2-hydroxypyrimidine (5M2HP), the enol form of deoxythymine [1,2]. Rotational contours were measured at 900 MHz (0.03 cm-1) resolution for the $S_1 \leftarrow S_0$ electronic origin and the three lowest-energy vibronic bands, assigned as the in-plane vibrations ν'_{6a}, ν'_{6b} and ν'_{14}. The 0_0^0 and the $6a_0^1$ vibronic bands exhibit methyl torsion sub-bands that arise from the near-degenerate methyl torsional ground states $0A''$ and $1E''$. Both the changes of rotational constants from the S_0 to the S_1 state and the S_0 and S_1 state torsional barriers were extracted from fits to the contours and torsional sub-bands. The 0_0^0 and the $6a_0^1$ bands are c-type polarized, identifying the longest-wavelength electronic transition of 5M2HP as $^1n\pi^*$.



[1] S. Lobsiger, H.-M. Frey and S. Leutwyler, *Phys. Chem. Chem. Phys*, **2010**, *12*, 5032.

[2] S. Lobsiger, P. J. Morgan, H.-M. Frey, D. W. Pratt and S. Leutwyler, in preparation.

Physical Chemistry **PC 55**

Supersonic Jet Spectroscopy of Medium-Strong Charge-Transfer Complexes

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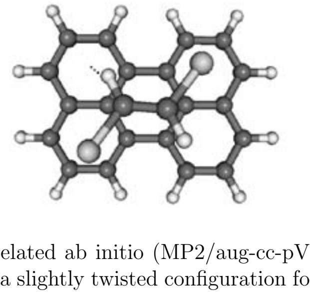
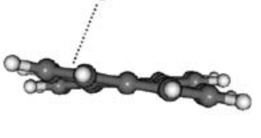
Charge-transfer or electron-donor-acceptor complexes are characterised by an electronic transition to an excited state with partial transfer of electronic charge. They are of great interest in the development of new conductive materials and superconductors. We investigated several charge-transfer complexes of perylene with chloroethenes such as trans-1,2-dichloroethene by means of resonant two-photon ionisation (R2PI) spectroscopy.





Correlated ab initio (MP2/aug-cc-pVTZ) and DFT-D calculations predict a slightly twisted configuration for the perylene moiety with a tilted trans-1,2-dichloroethene. These geometries exhibit both hydrogen-bonding and π-stacking characteristics.

Physical Chemistry **PC 56**

Excited-state dynamics of porphyrins-naphthalenediimide triads

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Over the past years, considerable efforts have been made in developing complex molecular architectures aimed to mimic the function of photosynthetic apparatus of plants and bacteria. Solar energy is collected by antenna systems (light-harvesting systems) and directed to the reaction center where it is used to produce a long-lived charge separated state thus being converted into chemical energy stored in carbohydrate molecules. Porphyrins and their derivatives play a central role in these complex natural systems, therefore much attention has been given to investigate the dynamics of their electronically excited states. In this work, we report an investigation of the excited state dynamics of two triads having either free-base (FB) or zinc-tetraphenylporphyrins (ZnTPP) covalently linked to naphthalenediimide (NDI) moiety using femtosecond transient absorption and fluorescence up conversion techniques. Our multichromophoric system is potentially suitable for both light harvesting and charge separation (CS). Beside multicromophoric absorption that covers a wide range of the spectrum, absorption cross-section is enhanced due to the presence of two identical units (ZnTPP and FBTPP). We have observed photo-induced intramolecular CS between ZnTPP, which acts as donor, and NDI as acceptor. All the details about the excited state dynamics will be discussed.

Physical Chemistry **PC 57**

Femtosecond Rotational Raman Degenerate Four-Wave Mixing Spectroscopy of Cyclopentane and d_{10}-Cyclopentane

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The accurate determination of the geometrical structure of nonpolar molecules is of great interest for chemistry. The technique of femtosecond rotational Raman degenerate four-wave mixing (fs-RR-DFWM) is well suited to fulfill this task. It was applied for the determination of highly accurate rotational and centrifugal distortion constants of cyclopentane and d_{10}-cyclopentane. Of special interest is the pseudorotational motion which was first described in 1947 [1].

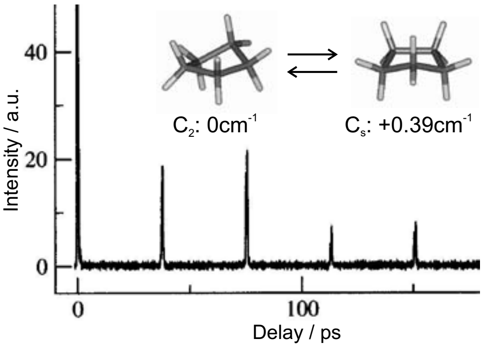

Fig. 1: Transient of Cyclopentane in a gas cell (298 K, p = 40 mbar) over the range of 0 - 175 ps [2].

[1] J.E. Kilpatrick, K.S. Pitzer, R. Spitzer *J. Am. Chem. Soc.*, **1947**, *69*, 2483.

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Physical Chemistry **PC 58**

IR/UV-Depletion Spectroscopy of 2-Pyridone·$(NH_3)_n$ Clusters

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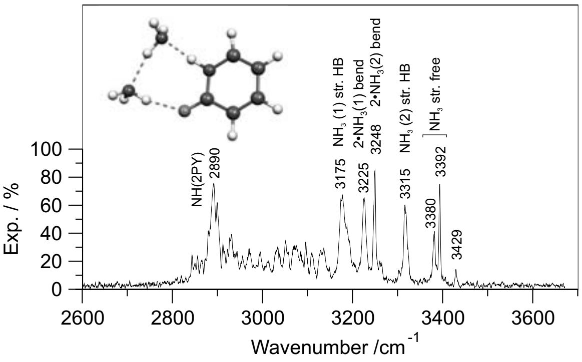
We measured IR-depletion spectra of 2-pyridone·$(NH_3)_n$ clusters with n=1-3 to investigate a possible proton and hydrogen atom transfer in the ground state, as has been predicted for 2-pyridone·$(NH_3)_5$ [1]. The N-H stretch frequency of the 2-pyridone unit shifts to the red with increasing number of NH_3 units attached to the 2-pyridone.



Performed B3LYP/TZVP calculations predict both the pyridone N-H and C=O bond lengths to increase with increasing number of attached NH_3 units. Both trends indicate incipient proton transfer, but no reaction is predicted up to n=3.

[1] M. Esboui, M. Nsangou, N. Jaidane and Z.B. Lakhdar , *Chem. Phys.*, **2005**, *311*, 277.

Physical Chemistry **PC 59**

Nonequilibrium vibration-mediated electron transfer between molecular absorbate and semiconductor nanoparticles

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This work reports on the importance of vibronic quantum states on the ultrafast interfacial electron transfer (ET) induced by light in dye molecules adsorbed at liquid/solid and solid/solid interfaces. The complete understanding of these processes is of great interest for the optimization of dye-sensitized solar cells (DSCs), characterized by dye molecules adsorbed onto a thin nanocrystalline semiconductor layer [1, 2]. Some theoretical models indeed predict important ET rate changes when the excited vibrational modes of donor molecules are populated [3]. The requirements for performing such measurements include a very precise infrared transient absorption as well as fast ET compared to the vibrational relaxation and intramolecular vibrational redistribution.

For this purpose, charge injection dynamics from organic dyes like azulene-2-carboxylic or organometallic complex such as $W(CO)_4(phen)$ absorbed onto TiO_2 (anatase) nanocrystalline layer will be investigated [4]. Femtosecond pump-pump-probe transient absorption setup will give us the opportunity to verify if the interfacial electron transfer can be optically controlled. In a second step, the calculation of the electron phonon coupling constant using theoretical models can help us understand the change in ET rate.

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Physical Chemistry **PC 60**

Melting point depression of brazing filler metals in a nanolayer system

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[2]Kirsten Soldering AG, Switzerland
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The joining of advanced metallic alloys is limited by high brazing or soldering temperatures. The nanoscale effect of melting point depression (MPD) offers a possibility of lowering the filler metal melting temperature without the compromises resulting from alloying. We have studied the MPD effect for nanolayer brazing fillers in a multilayer system, in which the layers of the brazing filler are separated by diffusion barrier layers (DBLs). The study shows that while the AlN diffusion barrier works optimal in combination with the AlSi brazing filler, it is not appropriate when aiming to decrease the melting point of AgCu brazing filler. An MPD of 230°C was observed for the 2.3 nm thick AlSi nanolayers in an AlSi/AlN nanomultilayer configuration.[1] For the 7.7 nm thick AgCu, a decrease of only 25°C for the melting point was observed for the AgCu/AlN nanolayer configuration. In this case, the eutectic AgCu brazing filler separates in two single phases and the local material interfaces Ag/AlN, Cu/AlN are formed. In-situ high temperature XRD studies show that while the 7.7 nm thin Cu nanophase layer is completely melted at temperatures below 600°C, the Ag nanophase starts to melt at a temperature of about 640°C and thus hinders the MPD of the brazing filler. Indeed, our investigations show, that the DBL material has to be chosen very carefully for the given brazing filler metal. The understanding of the internal and external interfaces in the material is crucial.

[1] V.Bissig, J.Janczak, Nanoscale effect-based melting point reduction for brazing filler metals, *Advanced Materials and Surfaces,* 09/10, p.8.

Physical Chemistry **PC 61**

NH$\cdots\pi$ hydrogen-bonding and large-amplitude tipping vibrations in jet-cooled pyrrole·benzene

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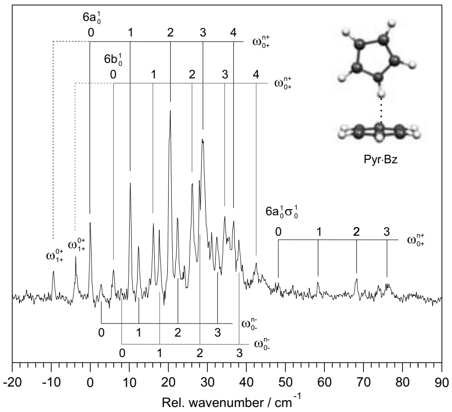
To understand the stabilization of proteins and peptides, the analysis of N-H$\cdots\pi$ unconventional hydrogen bonds is of great importance. We have investigated the infrared and UV spectra of the supersonic-jet cooled complex of pyrrole (Pyr) with benzene (Bz). DFT-D as well as SCS-MP2 and SCS-CC2 calculations predict a T-shaped C_s symmetric structure with an N-H$\cdots\pi$ hydrogen bond to the benzene ring. The NH stretch is redshifted by -59 cm^{-1} relative to that of bare pyrrole, indicating a moderately strong hydrogen bond. The UV spectrum shows long progressions in the 10 cm^{-1} ω' tipping vibration, in agreement with the change of the ω tipping angle predicted by SCS-MP2 and SCS-CC2 calculations.



[1] Ch. Pfaffen, D. Infanger, P. Ottiger, H.-M. Frey and S. Leutwyler, *PCCP*, **2011**, submitted.

Physical Chemistry **PC 62**

Vibrational bond-selective chemisorption of methane on Pt(111) studied by RAIRS

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Bond-selective control of a chemical reaction is an appealing intuitive strategy for laser controlled chemistry. The basic idea is to excite a local vibrational mode in order to break a selected bond in a polyatomic molecule, and thus alter the product yield of a reaction with several different possible pathways. Such bond-selective chemistry has been demonstrated for bimolecular reactions of vibrationally excited isotopologues of methane with chlorine atoms in gas phase [1-3] and more recently also for a gas/surface reaction of $CD_3H(\nu_1)$ on Ni(111) surface [4].

In this contribution, we describe the use of reflection absorption infrared spectroscopy (RAIRS) to detect the nascent product state distribution of a gas/surface reaction and apply the technique to probe for bond-selectivity in chemisorption reactions of different methane isotopologues on Pt(111). For example, we observe clear evidence for bond-selective dissociation of C-H stretch excited $CD_3H(\nu_1)$ on a Pt(111) surface. And we also present further experiments which probe to what extend the different vibrational modes of other methane isotopologues lead to bond-selective dissociation.

[1] J. P. Camden, H. A. Bechtel, D. J. A. Brown, and R. N. Zare, Journal of Chemical Physics **124**(3) (2006).
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Physical Chemistry **PC 63**

State resolved reactivity of methane on Pt(111)

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The activated dissociation of methane at metal surfaces is the rate-limiting step in steam reforming. Therefore it is important to unravel this reaction mechanism in detail. In addition, the understanding of such basic reactions is essential for the validation of theoretical models. In order to get detailed knowledge, we are studying quantum state resolved surface reactivity using molecular beam techniques with cw infrared laser. In this poster, we show the possibility of a combination of those techniques with newly installed reflection absorption infrared spectroscopy, which makes it possible to identify the nascent products of methane dissociation. State-selected various isotopic methane molecules were impinged onto Pt(111). From this study, we demonstrate that influence of vibrational excitation on dissociation and its bond selectivity.

Physical Chemistry **PC 64**

Dynamics of individual rotational states in a velocity filter for polar neutral molecules

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The dynamics of individual rotational states inside an electrostatic velocity filter have been investigated and characterized in detail by state-resolved detection of guided ammonia-molecules. Velocity distributions and guiding probabilities for individual rotational levels are presented and compared with trajectory calculations and a model to describe the state-dependent translational temperature.

Attempts to improve the filtering characteristics of an electrostatic guide through the use of a different field configuration are also presented.

Physical Chemistry **PC 65**

Bimolecular Photoinduced Electron Transfer in Room Temperature Ionic Liquids

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Photoinduced electron transfer (PET) is one of the most intensively studied processes and is involved in many different areas of science. Nevertheless the electron transfer theory for one of the easiest chemical reactions, derived by R.A. Marcus more than 50 years ago [1] is still not in total agreement with the experimental results. In nature, this process is carried out in complex systems and it is therefore easier to use well-known model compounds to earn a better understanding of the fundamental rules underlying the PET reaction.

In a totally different area of research, room temperature ionic liquids (RTILs) are handled as new green solvents. Due to the intrinsically different nature of RTILs it has to be investigated if PET in these solvents behaves the same or differently compared to "normal" dipolar solvents [2, 3].

We will present our results using well-known systems in which electron acceptor and donor are varied depending on the driving force.

Various femtosecond techniques are used for the investigation, e.g. transient absorption, fluorescence up-conversion and a newly built infrared spectroscopy setup.

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Physical Chemistry **PC 66**

A High Efficiency Panchromatic Squaraine Sensitizer for Dye-sensitized Solar Cells

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Dye-sensitized solar cells (DSCs), first reported in 1991 [1], are a promising low cost alternative to conventional inorganic semiconductor devices reaching up to 11% solar energy conversion efficiencies [2]. In solid-state DSCs, the liquid redox electrolyte, responsible for dye regeneration and hole transfer to the counter electrode, is replaced by a solid hole-transporting material (HTM). Due to incomplete pore filling of the mesoporous TiO_2 and the short diffusion length in the solid HTM, ssDSCs are restricted to thinner TiO_2 films. To overcome this limitation, dyes with high molar extinction coefficients are of great use. Here we report the use of the asymmetrical bis(indoline) squaraine sensitizer YR6 exhibiting a power conversion efficiency of 2.7% at AM 1.5G solar irradiation in a ssDSCs using the organic HTM, 2,2',7,7'-tetrakis(*N,N*-dimethoxy-phenylamine)-9,9'-spirobifluorene (spiro-MeOTAD). This shows an improvement upon current top-performing ssDSCs using squaraine dyes [3] and can be attributed to the panchromatic absorption of YR6. This results from a red shift of the absorption maximum and higher-energy bands arising from greater extended conjugation.

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Physical Chemistry **PC 67**

Reactive Molecular Dynamics study of sulfuric acid (H_2SO_4) Dissociation

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Sulfur is emitted mainly as sulfur dioxide (SO_2), which is oxidized to form sulfuric acid (H_2SO_4) [1]. This cycling between SO_2 and H_2SO_4 has been studied mainly because it plays an important role in the troposphere aerosol layer formation altering the chemical composition and influencing the course of aqueous reactions in clouds [2]. The mechanism and pathway involved in the photo-dissociation of H_2SO_4 have not been characterized yet. Some studies suggest that dissociation of H_2SO_4 is possible mainly by highly excited OH-stretching vibrational overtone in H_2SO_4 [3]. Thus, excitation of the higher OH-stretching vibrational overtone should provide sufficient energy for photo-dissociation to takes place.

Here we use a Reactive Molecular Dynamics (RMD) [4] to investigate vibrationally induced H_2SO_4 decomposition. Our result suggest a complete Internal vibrational energy redistribution (IVR), and it, appears to be important for the reaction takes place in picoseconds scale. The IVR would be increasing the coupling between different normal modes to produce the transition state, increasing excitation energy and the probability that the event occurs increase as well. This is an alternative mechanism that allow us to understanding the dynamics of the sulfuric acid photodissociacion in troposphere.

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Physical Chemistry **PC 68**

Multistage Zeeman Deceleration of Metastable Neon

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Multistage Zeeman deceleration employs time-dependent inhomogeneous magnetic fields to manipulate the translational motion of paramagnetic atoms and molecules in pulsed supersonic beams [1]. With this method, atomic and molecular samples with translational temperatures in the range 10-100 mK can be prepared which are ideally suited for applications in precision spectroscopy and studies of cold reactive collisions. In this contribution we shall present our latest generation of Zeeman decelerators. The decelerators are made of modules and can be easily extended or shortened depending on the mass and magnetic moment of the atoms or molecules to be decelerated [2, 3].

Using 91 deceleration solenoids, we slow Ne* atoms to velocities as low as 120 m/s, thereby removing up to 95% of the initial kinetic energy. We characterize the cold beam of Ne* atoms with a time-of-flight technique, which enables the complete reconstruction of the phase-space distribution of the decelerated sample and the characterization of the efficiency of the deceleration process. Implications on the design of optimal pulse sequences for the extension of the technique to other species will be discussed.

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Physical Chemistry **PC 69**

ROTATIONALLY RESOLVED SPECTROSCOPY OF THE ELECTRONICALLY EXCITED C AND D STATES OF ArXe AND KrXe

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Rotationally resolved (1+1') resonance-enhanced two-photon ionization spectra of the D and $C \leftarrow X\,0^+$ band systems of several isotopomers of ArXe and KrXe were recorded using a narrow-bandwidth VUV laser system [1] at a resolution of 0.01 cm^{-1} in the wave number range from 77000 cm^{-1} to 77400 cm^{-1} [2,3]. The analysis of the rotational structures enabled the characterization of the structure and dynamics of the $C\ \Omega = 1$ state of ArXe and the $D\ \Omega = 1$ state of KrXe [4]. In the case of Rg^{129}Xe and Rg^{131}Xe (Rg=Ar, Kr), the hyperfine structure could also be resolved and provided new information on these states, and on the nature of the perturbations [5,6]. Model potentials for the perturbing and perturbed excited states were constructed in an attempt to rationalize the spectroscopic data. The spectra of the C and D states of ArXe and KrXe reveal strong perturbations [4-6], and are subject to slow predissociation. Possible predissociation mechanisms and the possible origins of the perturbations are discussed and modelled theoretically.

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Physical Chemistry **PC 71**

Methane to Methanol Conversion on Cu-MOR

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Owing to the difficulty of methane partial oxidation, the success of converting methane to methanol at mild conditions over copper-exchanged zeolites [1] has been an inspiration to develop the biomimetic methane oxidation reaction route for a heterogeneous system. This process, however, suffers from strong sorption of the product on the catalyst surface such that a catalytic cycle could not be achieved. We pursued this lead and converted methane to methanol on Cu-MOR using water-assisted product desorption at 200°C. A catalytic cycle of activation-reaction-desorption-regeneration could be achieved by a feed switching cycle. Small amounts of methanol could be detected by online mass spectrometry, as well as GC analysis of the collected product. In situ infrared spectroscopy revealed the presence of a methoxy/methanol-like species on the surface of the catalyst after methane interaction. XAS spectroscopic measurements at the Cu K-edge showed a partial reduction of copper during methane conversion, which is similar to the behavior of copper to convert to a reduced state when covered with methanol.

[1] M.H. Groothaert, P.J. Smeets, B.F Sels, P.A. Jacobs, R. Schoonheydt, *J. Am. Chem. Soc.* **2005,** *127*, 1394.

Physical Chemistry **PC 70**

The Implications of Ultrafast Relaxation in Conjugated Polymers on the Functioning of Organic Solar Cells

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The femtosecond-resolved evolution of the emission spectrum of two conjugated polymers, P3HT and PCDTBT, is presented. The early relaxation processes (due to initial localization of the excitation, exciton formation, exciton diffusion and conformational relaxation) of the pristine materials, in film and solution, were investigated in detail with fluorescence up-conversion spectroscopy. Both P3HT and PCDTBT have been successfully used in organic bulk heterojunction (BHJ) solar cells. Ultrafast (<100 fs) charge separation (CS) between the polymer electron donor and a fullerene acceptor at their interface is the key step in the functioning of the BHJ solar cells. We therefore discuss the implications of the relaxation processes observed in the pristine polymers on the CS mechanism in the polymer:fullerene composites. Most relaxation occurs much slower than the <100 fs CS in the BHJ blend. In particular, excitons do not have time to diffuse to a polymer:fullerene interface prior to CS, in contrast with the commonly proposed picture. As CS occurs during the initial self-localization of the primary excitation, we therefore suggest that this excitation reaches the polymer:fullerene interface before it becomes spatially self-localized and bound within an exciton. The high initial mobility of the electron and hole directly after the π-π* interband transition and their delocalization (allowing quantum effects to assist the transport) could account for the observed ultrafast CS rate in BHJ blends.

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[2] Banerji et al., *J. Am. Chem. Soc.* **2010**, *132*, 17459

Physical Chemistry **PC 72**

Photocatalytic oxidation of alcohols on anatase TiO$_2$ nanosheets with highly exposed (001) facets

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Anatase TiO$_2$ nanosheets with highly exposed (001) facets have been synthesized and their catalytic reactivity has been evaluated by probing photocatalytic oxidation reaction of alcohols such as ethanol. Anatase TiO$_2$ (001) facets are known to be reactive in photo oxidation of organic molecules. In our previous work, our anatase TiO$_2$ nanosheets were found to be reactive in photodegradation of dye in aqueous solution. In this work, we employ them to study their interaction with alcohols in a pressure range of 10^{-6}–50torr. Our results indicate that our anatase TiO$_2$ nanocrystals are a good catalyst for the oxidation of alcohols. We also show that the photoactivity of the TiO$_2$ nanocrystals can be modified by doping nitrogen or by coadsorbing molecular oxygen.

Physical Chemistry **PC 73**

In situ investigation of TiO2 sensitization using a quartz microbalance and atomic force microscopy - A model system for dye-sensitized solar cells

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Dye sensitized solar cells (DSCs) are becoming a viable alternative to silicon solar cells for solar energy conversion due to their low cost and use of sustainable materials and relatively high efficiency. In fact, DSC efficiency of 11% have been attained through combination of a ruthenium-based dye and co-adsorbant sensitization [1]. However, the complex interactions between various metal organic, organic and co-adsorbents on the semiconducting scaffold has yet to be completely explained.

Herein, we employ a quartz microbalance with dissipation [2] to directly measure the mass uptake during sensitization of a flat TiO_2 film in liquid phase as a model system for understanding adsorption. We present in situ measurements of mass loading of ruthenium sensitizers (Z907), organic donor - pi bridge – acceptor (D-pi-A) dyes (Y123) and co-adsorbants (DPA, Cheno). In addition to precise quantification of the dye loading, we also study the adsorption / desorption dynamics on flat and mesoporous semiconductor DSC photoanodes.

Finally, these results are complimented by state-of-art atomic force microscopy (AFM) investigation of the self-assembled monolayer of sensitizer in the liquid phase [3] on the single molecule scale.

[1] Grätzel, M. *Acc. Chem. Res.* **2009**, *42*, 1788. [2] Rodahl et al. *Rev.Sci.Inst.* **1995**, *66*, 3924. [3]Kuna et al, *Nature Mat.* **2009**, *8*, 837.

Physical Chemistry **PC 74**

In Situ Growth of ZnO Nanowires in 3D ZnO Inverse Opals for Higher Efficiency Dye-Sensitized Solar Cells

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Dye-sensitized solar cells (DSCs) based on oxide semiconductors have emerged as a prominent candidate for efficient solar-energy conversion, both from a cost perspective as well as from fact that its components are abundant [1]. TiO_2 and ZnO are two similar wide band gap oxides that have been used in DSCs in the past. However, ZnO possesses a few significant advantages over TiO_2 that could increase the efficiency of DSCs over that of the state-of-the-art. For example, it offers higher electron mobility which is expected to improve electron transport and extraction [2]. Furthermore, it can be synthesized is a highly crystallized form at low temperature making it compatible with flexible polymer substrates. Finally, it can be grown into a large variety of nanostructures [2]. Herein, we present on the in situ growth of crystalline ZnO nanowires (NWs) into a 3D ZnO inverse opal backbone to be used as photoanode in DSCs. NWs offer direct transport pathways for photoexcited electrons enable better charge extraction. Additionally, using repeated atomic layer deposition they can be further branched by hydrothermal growth into high surface area "nanotree" structures [3] to increase dye loading and the resulting photocurrent. Finally, we show that the disordered nature of the backbone macropores improves light harvesting through light scattering. We will present the state-of-the-art DSC photovoltaic characterisitcs using this novel morphology.

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[2] Zhang Q., Dandeneau C. S., Zhou X., and Cao G., *Adv Mater* **2009**, *21*, 4087-4108

Physical Chemistry **PC 75**

Cross section of protein ions in the gas phase probed by electron impact ionization and dissociation mass spectrometry

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Electron-induced ionization/dissociation (EIID) of multiply charged proteins has been recently introduced as a soft ionization and fragmentation method to study primary structure of gaseous proteins and non-covalent protein complexes.[1] Here, we suggest to use EIID to probe protein structure beyond primary. Indeed, at electron energy of approximately 1 eV (electron capture dissociation conditions) electron wavelength is about 12 Angstroms which is comparable to protein size, whereas at electron energy of 100 eV (EIID conditions) electron wavelength is reduced to about 1.2 Angstroms resulting in higher spatial resolution. We thus demonstrate that EIID occurring specifically at high energy of electrons (20-100 eV) could be used for accurate protein structure characterization providing protein cross sections and ionization energies at different protein charge states.

The EIID experiments were performed on a high performance Fourier transform ion cyclotron resonance mass spectrometer (10 T FT-ICR MS at EPFL, Lausanne) equipped with ion-electron interaction cell located in a high magnetic field. Preliminary results obtained with EIID on isolated multiply protonated cytochrome c and myoglobin demonstrate three main ion groups appearing in the mass spectra in addition to the remaining precursor ions: charge-reduced species, charge-increased species and multiply charge-increased species, in agreement with previous work.[1] The obtained relative cross sections for +15 cytochrome C and +21 myoglobin ions correspond, within the method error, to their relative geometrical cross sections, as estimated by ion mobility measurements. We aim to increase the accuracy of the method and extensively compare protein cross sections provided by EIID and ion mobility mass spectrometry.

[1] Zubarev and Yang, *Angew. Chem.-Int. Edit.* **2010**, *49*, 1469-1441.

Physical Chemistry **PC 76**

Microfluidic array cytometer based on refractive optical tweezers for parallel trapping, imaging and sorting of individual cells

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Analysis of genetic and functional variability in populations of living cells requires experimental techniques capable of monitoring cellular processes such as cell signaling of many single cells in parallel while offering the possibility to sort interesting cell phenotypes for further investigations. Although flow cytometry is able to sequentially probe and sort thousands of cells per second, dynamic processes cannot be experimentally accessed on single cells due to the sub-second sampling time. Cellular dynamics can be measured by image cytometry of surface-immobilized cells, however, cell sorting is complicated under these conditions due to cell attachment. We here developed a cytometric tool based on refractive multiple optical tweezers combined with microfluidics and optical microscopy. We demonstrate contact-free immobilization of more than 200 yeast cells into a high-density array of optical traps in a microfluidic chip. The cell array could be moved to specific locations of the chip enabling us to expose in a controlled manner the cells to reagents and to analyze the responses of individual cells in a highly parallel format using fluorescence microscopy. We further established a method to sort single cells within the microfluidic device using an additional steerable optical trap. Ratiometric fluorescence imaging of intracellular pH of trapped yeast cells allowed us on the one hand to measure the effect of the trapping laser on the cells' viability and on the other hand to probe the dynamic response of the cells upon glucose sensing.

Physical Chemistry **PC 77**

New perspectives in lipophilicity determination of highly lipophilic compounds.

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The partition coefficient, log *P*, is an indispensable tool in predicting the transport and activity of drugs [1]. It is generally held that very lipophilic compounds are preferred target for metabolism, often leading to high clearance values and high plasma protein binding. Therefore determination of lipophilicity is important but still a challenge in pharmaceutical as in cosmetic field. The advantages of RPLC techniques for fast lipophilicity measurements are well recognized [2]. A set of 55 compounds with very different lipophilicity was selected. Different strategies based on use of UHPLC and HPLC have been chosen for the evaluation of extraordinary lipophilicity; a method was developed with 100-mm *Hypersil GOLD CN* column. Characterization of this reversed-phase system was attempted by estimating characteristic interaction constants for the stationary phase based on linear solvation energy relationships. Log k_w for each compounds was correlated with solute properties, namely intrinsic molecular volume and the solvatochromic parameters π^* (dipolarity/polarizability), β (H-bond acceptor basicity) and α (H-bond donor acidity). Interesting perspectives have been highlighted, in terms of good balance between time saving and accuracy compared to the other HPLC methods for the measurement of lipophilicity of highly lipophilic compounds.

[1] S.C. De Vito, in *Handbook of Property Estimation Methods for Chemicals*, eds Boethling, D. Mackay CRC Press: Boca Raton, **2000**, 261.
[2] S. Martel, D. Guillarme, Y. Henchoz, A. Galland, J. L. Veuthey, S. Rudaz, P. A. Carrupt, in *Molecular Drug Properties: Measurement and Prediction*; eds. Mannhold, R. , Wiley-VCH: Weinheim, Germany, **2007**, 331.

Physical Chemistry **PC 79**

Catalytic decomposition of guanidnium formate on noble metal-doped TiO_2-catalysts

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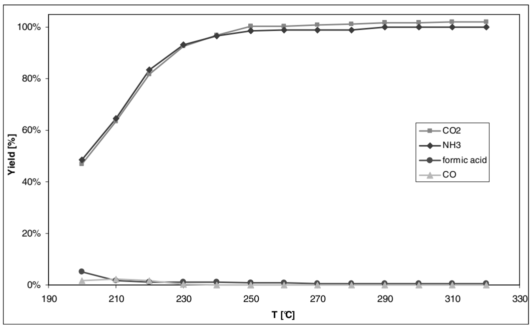
Selective catalytic reduction (SCR) of nitrous oxides in exhaust gas by NH_3 relies on an aqueous urea solution to generate ammonia in mobile applications. However, this aqueous solution has several drawbacks concerning NH_3-capacity and stability. Alternatives to urea have been evaluated, of these, guanidinium formate emerged to be of particular interest [1].

While the guanidinium cation could be decomposed to NH_3 and CO_2 on well-known TiO_2-catalysts, the formate anion yielded formic acid or decomposed to CO. Side reactions of formic acid with NH_3 led to undesired compounds. Doping of TiO_2 with noble metals resulted in complete decomposition of formic acid to CO_2, while NH_3 was not oxidized.



Decomposition of an aqueous 60% guanidinium formate solution on a 1.5% Au/TiO_2 catalyst (GHSV = 14900 h^{-1}, 10% O_2, 5% H_2O)

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Physical Chemistry **PC 78**

Perturbations in the Spectra of High Rydberg States

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Rydberg states of principal quantum number $n \gg 50$ have been prepared by irradiation of an atomic beam of xenon with vacuum ultraviolet (VUV) radiation. Narrowband submillimeter-wave (THz) radiation was then used to record spectra of transitions from these Rydberg states to higher or lower-lying Rydberg states. The transitions were detected by selective field ionization and recording either the electrons or the ions, the latter offering the advantage of mass selection.

Rydberg states of high principal quantum number are extremely sensitive to their environment, which can be exploited to characterize the experimental conditions under which the spectroscopic measurements are carried out [1]. The high resolution achieved in the experiments (better than 100 kHz) enabled the study of the spectral lineshapes and line positions in dependence of weak electric (down to below 100μV/cm) and magnetic fields (down to a few μT), and of the density of Rydberg atoms and ions generated in the experimental volume. The experiments rely on the use of a pulsed, broadly tunable, laser-based source of THz radiation [2] for survey scans, and of a phase- and frequency-stabilized submillimeter-wave backward-wave oscillator-based radiation source [3] for precision measurements.

To illustrate the use of these sources, we present the results of the spectroscopic investigations of the hyperfine structure of ^{129}Xe Rydberg states.

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[3] M. Schäfer, M. Andrist, H. Schmutz, F. Lewen, G. Winnewisser and F. Merkt *J. Phys. B: At. Mol. Opt. Phys.*, **2006**, *39*, 831.

Physical Chemistry **PC 80**

Manipulating Rydberg atoms close to surfaces

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With the goals of (i) studying molecular collisions at low temperature or with a high degree of control over collision energies, and (ii) studying the interaction between trapped Rydberg atoms and a variety of surfaces, we are currently developing a new generation of chip-based, Rydberg-Stark deceleration experiments. This work builds on the recent demonstration of methods by which to decelerate and manipulate the translational motion of Rydberg atoms in the gas phase using static and time-varying inhomogeneous electric fields [1–3], that has led to the experimental demonstration of two- and three-dimensional electrostatic trapping of Rydberg atoms [4,5] and molecules [6].

Recent studies of the effects of blackbody radiation on electrostatically trapped ensembles of hydrogen Rydberg atoms [7] have highlighted the role of blackbody radiation in state-changing and photoionization in these experiments. To control these process, our new generation of chip-based, Rydberg-Stark decelerators are constructed to operate in an environment which is cooled to 4 K. The design and operation principle of these decelerators will be presented along with experimental studies of the sensitivity of Rydberg states of atomic hydrogen, with principal quantum numbers in the vicinity of $n = 30$, to blackbody radiation at temperatures between 4 K and 20 K.

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