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Physical Chemistry, Talk **501**

Can One Measure Transverse Relaxation Rates of Protons in NMR?

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In Nuclear Magnetic Resonance (NMR), measurements of transverse relaxation times T_2 of protons are challenging due to modulations arising from homonuclear *J*-couplings. The suppression of these echo modulations in time domain is a counterpart to the decoupling of multiplets in frequency domain.

We compare different techniques to circumvent this problem:

- Spin-lock sequences to measure $T_{1\rho}$
- Carr-Purcell-Meiboom-Gill (CPMG) echo trains with moderate radiofrequency (*rf*) pulses [1]
- Perfect Echoes to refocus homonuclear *J*-couplings [2,3]

All techniques can suppress echo modulations and lead to exponential decays, but the apparent transverse relaxation times T_2 are not always identical. This depends on whether a pulse sequence is *refocusing* or *locking* the homonuclear *J*-couplings. While a continuous-wave *rf*-field can *lock* the inphase magnetization I_x, *refocusing* may allow a partial conversion into antiphase magnetization $2I_yS_z$. The relaxation times of these two coherences are usually not identical and the antiphase magnetization decays faster.

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Physical Chemistry, Talk **502**

Investigation of intramolecular vibrational energy flow in polyatomic molecules by the femtosecond pump-probe technique

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Intramolecular vibrational energy redistribution (IVR) is one of the most important primary processes for molecular kinetics [1, 2]. Its understanding is important for planning experiments on controlled mode-selective chemistry. IVR processes can be experimentally investigated indirectly via the analysis of highly resolved IR spectra [1, 2], or directly studied by time-resolved spectroscopy [3], the approach used here. In our pump-probe experiments in the gas phase we excite for example the first overtone range of CH-stretching vibrations with a 100 fs pump pulse, and follow the IVR dynamics with a 100 fs probe pulse [3]. The spectral resolution of the probe pulse allows us to investigate effectively the depopulation of initially excited states and the population transfer to other isoenergetic combination states. Investigations of methane and propyne derivatives show that the timescales for IVR processes strongly depend on the specific intramolecular couplings. Depending on the initial excitation in the same molecule for instance with acetylenic and alkylic CH chromo-phores the time scales for IVR range from the sub-100 fs range to the pico- and up to the nanosecond, perhaps even the microsecond range, in agreement with high resolution spectroscopic studies (see [1,2]).

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Physical Chemistry, Talk **503**

Bimolecular Photoinduced Electron Transfer in High Viscous Media: Spurious Observation of the Marcus Inverted Region.

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Over the last decade, there have been many reports on the observation of the Marcus Inverted Region (MIR) in bimolecular photoinduced electron transfer (BPET) in micellar media and room temperature ionic liquids.[1] In all these studies, the electron transfer rate constant was extracted from a simple Stern-Volmer (SV) analysis of the fluorescence data. However, we have shown recently that in viscous media this approach leads to rate constants too large by orders of magnitude.[2]

To check if also the MIR is a result of the simplistic analysis, we have performed a detailed investigation of the effect of viscosity on the dynamics of BPET using time-resolved and stationary fluorescence. When performing a simple SV analysis of the nanosecond time-resolved and steady-state fluorescence data, we found that the inversion effect arises as the viscosity is increased above 2 cP. However, when analysing the femtosecond fluorescence data, we found that the static electron transfer rate constant does not exhibit any inversion effect independently of the viscosity. Furthermore, by accomplishing an assay of all the data with a model that accounts for the time dependence of the quenching rate, we found that neither the static quenching rate constant nor the diffusional rate constant show an inversion effect. We will demonstrate that the spurious observation of the MIR is due to a too simplistic analysis of quenching data combined with the use of chromophores with different fluorescence lifetimes.

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Physical Chemistry, Talk **504**

Azide-water coupling measured by 2-color 2D-IR spectroscopy

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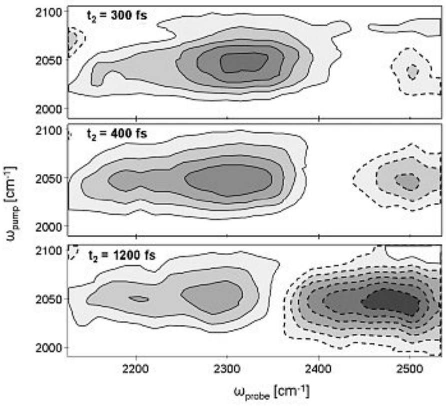
We present 2-color 2D-IR spectra of NaN_3 in neat D_2O [1]. A cross-peak between the ion’s asymmetric stretch vibration and the OD-stretch vibration of surrounding water molecules is observed with the main origin of the signal being due to population transfer between the azide and water directly hydrogen bonded to it. The exceptionally broad excited state absorption so far has been only observed in ice Ih [2], where it was linked to hydrogen bond strength between two water molecules. The measured 2-color 2D-IR spectra thus suggest the hydrogen bond strength between azide and surrounding water molecules is of the same order as in ice Ih lattice.



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Physical Chemistry, Talk **505**

Peptide Backbone Fragmentation Pathways in Electron Capture and Transfer Dissociation Mass Spectrometry

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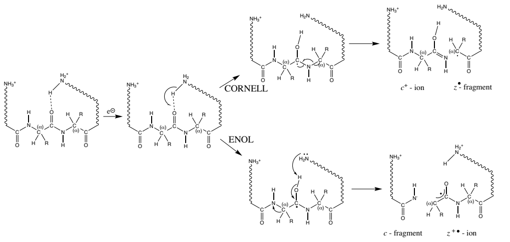
Peptide N-C(α) backbone bonds are preferentially ruptured in electron capture and transfer dissociation (ECD and ETD) mass spectrometry through the attachment of electrons to positively multiply charged analyte molecules in the gas phase. The resulting intermediate charge reduced species, being radical cations, dissociate by fast fragmentation processes, yielding *c*- and *z*-type products, see Figure. The generally accepted mechanism, the "Cornell" pathway, results in N-C(α) cleavage occurring to the right-side of a hydrogen acceptor carbonyl oxygen located in the backbone. Here, we show that an alternative proposal, the "enol" pathway, where cleavage occurs to the left-side of the hydrogen atom-solvated backbone carbonyl group, not only is energetically viable, but denotes the preferred route to *c*- and *z*-product formation for a majority of the Ala_5-Lys conformers studied via density functional theory. The enol pathway provides the lowest energy routes to several of the product ions observed in ECD/ETD mass spectra of H-$(Ala)_n$K-OH model peptide dications, where *n*=2-5.



Physical Chemistry, Talk **506**

Structure of Formic Acid in the Liquid Phase

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The electronic structure of formic acid (HCOOH) and of the formate ion ($HCOO^-$) has been investigated in aqueous solutions over a pH range of 1.88-8.87 using a combination of in situ X-ray photoelectron spectroscopy (XPS), in situ partial electron-yield X-ray absorption spectroscopy (PEY XAS), and density functional theory (DFT). The carbon 1s XPS measurements reveal a chemical binding energy shift of -1.3 eV for deprotonated $HCOO^-$ compared with neutral HCOOH in aqueous solutions due to increased electron density on the carbon atom that results from a shortening of the C—O bonds and the delocalization of the negative charge across the O—C—O bonds, and allows for the protonation state of formic acid in aqueous solutions to be easily identified using XPS. Such distinction between neutral HCOOH and deprotonated $HCOO^-$ in aqueous solutions cannot be made based solely on the respective carbon K-edge PEY XA spectra. Independent of pH the C1s → π* state excitations occur at 288.0 eV photon energy and may lead to the incorrect conclusion that the energy levels of the π* state are the same for both species in aqueous solutions. The DFT calculations are consistent with the experimental observations only when a dielectric solvation field and explicit solvation are both included in the model, and show a shift to higher energy for both the occupied C1s and unoccupied π* orbitals of deprotonated $HCOO^-$ compared to neutral HCOOH in aqueous solutions.

Physical Chemistry, Talk **507**

π-Conjugated Donor-Acceptor Systems as Metal-Free Sensitizers for Dye-Sensitized Solar Cell Applications

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Metal-free organic sensitizers for dye-sensitized solar cells exhibit lower photoconversion efficiencies (< 10 %) than corresponding ruthenium complexes (11.7 %)[1,2] but they can be synthesized rather inexpensively and their optical properties can be tuned by molecular design. Among these, structures implementing π-conjugated donor-acceptor (D-π-A) architectures exhibit growing interest due to the tunability of their electronic properties by their conjugation length.

Ultrafast techniques such as femtosecond and nanosecond transient absorption spectroscopy allow studying the dependence of the charge carrier dynamics in fully organic dye/TiO_2 systems on parameters such as donor-acceptor distance, π-conjugation length and coupling to TiO_2 by different anchoring groups. We have shown that a sensitive interplay between the dyes' building blocks governs the charge injection/recombination and dye regeneration rates and that they do not necessarily follow an exponential distance dependence as given by $k_{CT} = k_0 \, x \, exp(-\beta r_{DA})$ as often stated for dyes of D-π-A architecture.[3,4]

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Physical Chemistry, Poster Talk **508**

Photoinduced charge transfer processes in polycyclic aromatic hydrocarbon dyads

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We are investigating the excited-state dynamics of various bichromophoric systems composed of two polycyclic aromatic hydrocarbons both bridged and directly linked. One of them, a bridged perylene-perylene (Pe-Pr-Pe) system, was specially designed in order to find out whether photoexcitation could be at the origin of the symmetry-breaking (SB) charge separation (CS) process[1]. Photoinduced SB 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.

Clear evidence of SB CS in our molecule 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 toward the excited Pe unit, are operative and that their associated rate constants differ by less than a factor 2. The reason for the absence of preferred CS direction and the conditions where preferred direction could be observed will be discussed.

This study has been extended to systems with two different chromophores where, upon photoexcitation, we observe structural changes, energy and electron transfer between the units. These systems will also be presented.

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Physical Chemistry, Poster Talk **509**

Improving photocurrent onset potential in ultrathin hematite films using a combination of Nb_2O_5-, SiO_x-underlayers and a Ga_2O_3 overlayer

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The production of hydrogen by solar water splitting in photo-electrochemical cells converts solar energy into a clean and transportable fuel. For this application, α-Fe_2O_3 is a well-studied photo-electrode material as it is abundant, chemically stable under the applied conditions and has a favorable band-gap of ~2.0 eV. However, its performance as a photoanode is limited by its poor electronic conductivity and short carrier lifetime resulting in a short hole diffusion length. Presently reached solar to hydrogen energy conversion efficiencies (SHCE) are much lower than the theoretical maximum of ca. 15%. A promising approach to enhance the SHCE is the application of nanostructuring techniques and interfacial engineering.[1] Recent studies on a Ga_2O_3 overlayer [2] and a SiO_x underlayer [3] showed a reduction of losses in form of a cathodic shift of the photocurrent onset potential. In addition, deposition of an extremely thin layer of hematite on a high surface area scaffold allows the photogeneration of holes in close proximity to the semiconductor-liquid junction, thus, reducing recombination losses. Here, we present a systematic study on ultrathin hematite films with different surface treatments applying Nb_2O_5 and SiO_x underlayers, a Ga_2O_3 overlayer, as well as suitable combinations of under- and overlayers examined at different annealing temperatures. The investigated underlayers enhance the photocurrent and show a remarkable cathodic shift in the photocurrent onset potential. In combination with a Ga_2O_3 overlayer the onset potential could be minimized to ~0.4 V anodic of the semiconductor flat-band potential, representing our best reported photocurrent onset potential for ultrathin (<20 nm) hematite films without applying a cobalt-catalyst to date.

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Physical Chemistry, Poster Talk **510**

Towards Understanding Allosteric Dynamics Through Ultrafast IR Spectroscopy

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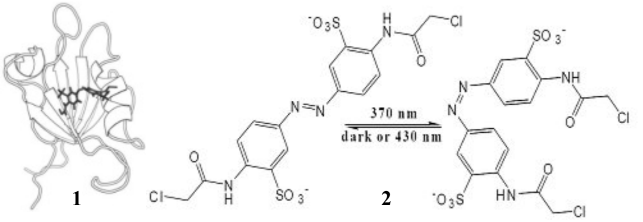
Allosteric interactions are an important regulatory mechanism to modulate enzyme activities and binding affinities. However, little is known about the dynamics and the timescales of allosteric transitions. To investigate this, we have covalently bound a photoswitch [1] to a PDZ domain [2] **1** which shows allosteric properties [3]. Illumination leads to an isomerization of the switch **2** and mimics the allosteric conformational transition of the domain.



With UV-pump IR-probe spectroscopy we can probe the kinetics of this transition over tens of microseconds with picosecond time resolution. Through coupling a laser into an NMR spectrometer, we will determine structural information and equilibrium dynamics of the protein with the photoswitchable linker in both conformations.

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Physical Chemistry, Poster Talk **511**

Investigation of $TiCl_4$ treatment on carrier dynamics in solid-state dye-sensitized solar cells studied by time-resolved spectroscopy

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Solid-state Dye-Sensitized Solar Cells (ssDSCs) are a promising and challenging alternative to conventional DSCs based on volatile and/or corrosive liquid electrolytes [1]. Although these systems, which use organic hole-transport materials (HTM) such as spiro-OMeTAD, are now reaching 7% PCE, additional efforts need to be invested in order to reach the same efficiencies as their liquid equivalent. It has been observed that the cell efficiency is increased by an additional treatment by $TiCl_4$, which modifies the TiO_2 surface [3]. The actual effect of this fabrication step on the solid-state cell and the mechanism involved, however, are still unclear.

Based on kinetic studies obtained by femtosecond and nanonsecond transient absorption spectroscopy, this surface treatment was shown to affect the dynamics of all charge carriers in the cell compared to non-treated films: electron injection, hole injection and charge recombination. Herein, we propose a model describing the interaction at the interface between TiO_2, the dye-sensitizer and spiro-OMeTAD. Results also emphasize the importance of controlling the contact at the heterojunction between the HTM and the sensitized semiconductor.

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Physical Chemistry, Poster Talk **512**

Investigating the pseudorotation of cyclopentane by femtosecond rotational Raman coherence spectroscopy

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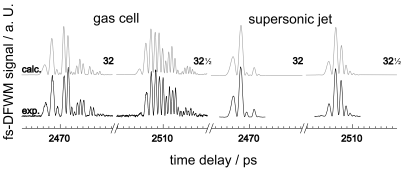
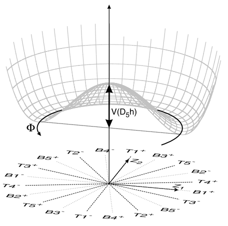
To obtain highly accurate rotational constants for the nonpolar molecule cyclopentane (C_5H_{10}), we used femtosecond time-resolved rotational Raman coherence spectroscopy. To improve the accuracy, measurements in a gas cell at room temperature were combined with a pulsed supersonic jet [1]. Assuming the pseudorotational/radial potential, shown in Fig. b, the most accurate ground state rotational constant, $B_0 = 6484.930(11)$ MHz, for cyclopentane was obtained. A tiny rotation-pseudorotation coupling constant $\alpha_{pseudo} = -0.704(14)$ kHz indicates a negligible effect of the population of pseudorotational states on the rotational coherence.



(a) Comparison of gas cell and jet measurements



(b) Two-dimensional double minimum potential

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Physical Chemistry, Talk **513**

Improving the Mean Localization Precision in Sub-Diffraction Fluorescence Blink Microscopy by Tuning the Photophysics of an Oxazine Fluorophore

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Fluorescence microscopy has become essential to biological research and novel sub-diffraction imaging techniques, among which blink microscopy, allow optical resolutions of only a few tens of nanometers to be achieved. Blink microscopy relies on the chemically-induced stochastic photoswitching of fluorescent probes between bright and dark states to construct sub-diffraction images and has the advantage of being amenable to most conventional fluorophores [1].

Whereas the fluorescence quantum yield of many photoswitchable fluorophores with excitation wavelength below 600 nm is larger than 0.7, common near-infrared emitters used for bioconjugation hardly reach a fluorescence quantum yield higher than ~0.3, leaving room for an improvement in brightness by a factor up to 3. At constant radiative rate, such improvement in fluorescence quantum yield could potentially translate to an almost two-fold gain in localization precision, since the latter directly depends on the square root of the number of photons detected for each molecule.

Atto655 is a near-infrared fluorescent probe commonly used in blink microscopy [1] with a fluorescence quantum yield of 0.3 in water. Here we show that it is possible to double the fluorescence quantum yield of this oxazine dye in aqueous solution and bring it even close to unity in solvents compatible with fixed biological samples. Accordingly, we demonstrate an improvement in mean localization precision by blink microscopy imaging of the G protein-coupled receptor CCR5 in the filopodia of mammalian cells.

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Physical Chemistry, Talk **514**

Efficient Laser Induced Population Transfer in NH_3 – The First Step towards the Measurement of the Parity Violating Energy Difference $\Delta_{PV}E$ between Enantiomers of Chiral Molecules

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Electromagnetic quantum chemistry predicts the ground state energies of enantiomers of chiral molecules to be exactly equal by symmetry. According to our current understanding, however, the electroweak interaction breaks this symmetry and thus electroweak quantum chemistry predicts a slight energy difference $\Delta_{PV}E$ of the ground states of enantiomers, corresponding to a reaction enthalpy $\Delta_{PV}H_0^{o}$ for the stereomutation [1-5]

$$R = S, \qquad \Delta_{PV}H_0^{o} = N_A\,\Delta_{PV}E \qquad (1)$$

The theoretical calculation of the parity violating energy difference in molecules is now well established and reveals values between 10^{-11} – 10^{-9} $Jmol^{-1}$ [2-5]. But its experimental verification is still missing. This energy difference can be measured by challenging high-resolution spectroscopy or in a time resolved experiment proposed 25 years ago [1]. We present an experimental scheme and the first experimental results towards the detection of the parity violating energy difference in molecules by the proposed technique.

In the experiment a two photon absorption/stimulated emission process is followed by an interaction free evolution period and a sensitive multiphoton ionization detection. To exclude any perturbation during the evolution period the experiments are performed in a molecular beam. First experimental results are shown for the two step population transfer for the achiral NH_3.

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Physical Chemistry, Talk **515**

Dissociative electron attachment in molecules from alkynes family

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The absolute cross sections for formation of ions by **dissociative** electron attachment (DEA) to methylacetylene ($HCCCH_3$), to deuterated methylacetylene ($HCCCD_3$) and as well dimethylacetylene (CH_3CCCH_3) have been measured by spectrometer with trochoidal electron monochromator combined with quantitative time-of-flight mass spectrometer [1].

This work has been motivated by role of these molecules in interstellar media and upper planetary atmospheres [2, 3], as well as by previous studies of acetylene in our laboratory [1, 4]. The main product from low-energy dissociative electron attachment to methylacetylene and deuterated methylacetylene is the $(M-1)^-$ anion corresponding to abstraction of one hydrogen atom. The $(M-1)^-$ peak cross section is lower than that in acetylene. As expected, C_2H^- ions have not been formed, which confirms that the $C\text{-}CH_3$ bond is not cleaved by low-energy electrons. This has been verified in DEA to dimethylacetylene, where no fragments except H^- have been detected. Possible origins of this effect are discussed.

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Physical Chemistry, Talk **516**

High-precision measurements of the ionization and dissociation energies of molecular hydrogen

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Molecular hydrogen is the most important system for testing quantum mechanics and quantum electrodynamics in molecules. The comparison of experimental and theoretical values of the dissociation energies of H_2, HD, and D_2 has a long history and led to a quantitative understanding of chemical binding. The most precise determination of the dissociation energies was carried out recently by measuring the ionization energies with a relative accuracy of 3×10^{-9} and combining the results with known energy spacings in H, D, H_2^+, HD^+, and D_2^+. The ionization energies were determined by measuring three intervals independently: the $1s\sigma\,X \rightarrow 2s\sigma\,EF$ interval [1], the $2s\sigma\,EF \rightarrow n$p ($n \approx 60$) interval [2-4], and the electron binding energy of the np Rydberg states [3-6]. All values are in agreement with the results of the latest *ab initio* calculations [7,8] within the uncertainty limit of 30 MHz (0.001 cm^{-1}). New measurements with an improved accuracy will allow for a more stringent test of future *ab initio* calculations. We will discuss a new scheme for an experiment aiming at sub-MHz accuracy and present the results of preliminary measurements.

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Physical Chemistry, Talk **517**

High-resolution photoelectron spectroscopic investigation of cyclopropene (c-C_3H_4) and its deuterated isotopomers

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The spectroscopic information available on the cyclopropene radical cation is limited to that contained in low-resolution He I photoelectron spectra [1,2]. To better characterize the structure of this cation, we have recently measured high-resolution pulsed-field-ionization zero-kinetic-energy photoelectron spectra of c-C_3H_4 and several of its deuterated isotopomers in the vicinity of the adiabatic ionization threshold. Our new data include fully rotationally resolved spectra of the origin band of the $\widetilde{\mathrm{X}}^+ \leftarrow \widetilde{\mathrm{X}}$ transition of c-C_3H_4 and spectra of the low-vibrational levels of c-$C_3H_4^+$ and the deuterated isotopomers recorded at lower resolution. Because our efforts at synthesizing the partially deuterated isotopomers always resulted in mixtures of several isotopomers, differing in their number of D atoms and in the location of these atoms, the analysis of the isotopic shifts turned out to be challenging. Combining the information contained in the rotational structure of the origin band of c-$C_3H_4^+$ with the ionization energies of the isotopomers measured by photoionization mass spectrometry and the vibrational structure observed in the PFI-ZEKE spectra of the mixtures of deuterated isotopomers, we were able to draw conclusions on the structure of the cyclopropene radical cation based solely on experimental data and on the mechanism of the reaction by which c-C_3H_4 is produced. The adiabatic ionization energy of c-C_3H_4 was determined to be 77931.8(5) cm^{-1}.

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Physical Chemistry, Talk **518**

Shape and dipole-bound resonances in acrylonitrile

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The interest in acrylonitrile stems from its occurrence in outer space [1] and because it is widely used as a starting material to make polymers. It has a dipole moment of 3.86 D [3], has been shown to support dipole-bound states [2], with a measured binding energy of 6.9 meV [3]. Dissociative electron attachment for acrylonitrile has been measured [4]. Vibrational excitation by electron impact has been measured for acrylonitrile molecules adsorbed on Cu [5].

We measured the elastic and vibrationally inelastic differential cross sections in acrylonitrile at the scattering angle of 135°. Three shape resonances, due to temporary occupation of three π* orbitals, are expected in acrylonitrile. Qualitative arguments based on the attachment energies of ethene (1.9 eV) and HCN (2.5 eV) lead to expectation of roughly 2.2 ± 2 eV, i.e., 0.2 eV and 4.2 eV for π_1^* and π_3^* (the in-phase and out-of-phase combinations of the vinyl and cyano π* orbitals) and about 2.5 eV for π_2^* (the in-plane π* orbital of the cyano group). The π_2^* and π_3^* resonances appear as broad bands at 2.9 eV and 4.4 eV, below 1 eV we observe complex narrow structures which must be due to either boomerang structure of the π_1^* shape resonance, or to vibrational Feshbach resonances.

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Physical Chemistry, Talk **519**

High-harmonic spectroscopy of oriented OCS molecules

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High-harmonic spectroscopy (HHS) is an emerging tool for studying the electronic structure and dynamics of molecules on femtosecond to attosecond time scales. Performing such measurements in the molecular frame will greatly extend the opportunities of HHS of polar molecules, which requires the orientation of the sample.

We report the observation of even-order high-harmonic generation from OCS molecules, which were impulsively aligned and oriented using a femtosecond laser pulse and its superimposed second harmonic.[1] Odd harmonic emission is found to be insensitive to the degree of orientation, but modulates with the degree of axis alignment, in agreement with calculated photorecombination dipole moments. These odd harmonics reflect the sum of electric fields emitted by the recollision from the two sides, whereas the even harmonics reflect the difference. Thus the even harmonics only appear around the full revivals of the rotational dynamics. We further compare the shape of the even and odd harmonic spectra with our calculations and determine the degree of orientation. Moreover, we demonstrate perfect coherent control over the intensity of the even harmonics through the sub-cycle delay of the two-color field by tilting a calcite plate in the pump beam which controls the group delay of the fundamental and its superimposed second harmonic.

Our results show that orientation adds an important new aspect to high-harmonic spectroscopy by giving access to additional aspects of the electronic structure and constituted the first step towards measuring charge migration in polar molecules on the attosecond time scale.

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Physical Chemistry **520**

Photoinduced energy and electron transfer in porphrins-naphthalenediimide multichromophoric systems

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Over the past years considerable efforts have been made in developing complex molecular architectures for mimicking the function of photosynthetic apparatus of plants and bacteria. Solar energy is collected by light-harvesting system 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 carbohydrates 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) unit using femtosecond transient absorption and fluorescence up conversion techniques. Beside multichromophoric absorption that covers a wide range of the spectrum, the absorption cross-section is enhanced due to the presence of two identical porphyrin units. Photoinduced intramolecular charge separation (CS) between porphyrin, which acts as a donor and NDI as an acceptor occurs in polar solvents. An ultrafast charge recombination follows, allowing the observation of the hot ground state absorption. We are also studying more complex systems with four identical porphyrin and one NDI unit, which are potentially suitable for both light harvesting and CS. In these molecules the excitation energy located on the $ZnTPP$ or $FbTPP$ is transferred to the central NDI unit and followed by intramolecular CS. The excited state dynamics of all these systems and their solvent polarity dependence will be discussed.

Physical Chemistry **521**

Ultrafast Bulk Investigations on the Photo-Induced Electron Transfer between Tryptophan and the Potential Interfacial Probe Lucifer Yellow

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Many electron transfer processes occurring in nature take place at the interface between an aqueous and a hydrophobic medium. As some of these processes might be of interest for energy storage purposes, much effort has been put into trying to reproduce them artificially. Although considerable progress was made in this field, the knowledge about the factors influencing the charge separation efficiency at liquid/liquid interfaces is still poor.

The main reason for the lacking knowledge about the properties of liquid/liquid interfaces is that they are difficult to access experimentally. A powerful option is to take recourse to non-linear spectroscopic techniques, like time-resolved second harmonic generation (tr-SHG), which, due to its interface selectivity, has proven a valuable tool for the purpose of studying liquid interfaces during the last decades, and is readily available in our lab [1,2].

Its interesting properties [3] make the water-soluble naphthalene monoimide derivative lucifer yellow (LY) a suitable candidate for exploring interfacial electron transfer. Here we present the ultrafast bulk investigations on the photo-induced electron transfer between LY and the amino acid tryptophan, which are needed for comparison in order to be able to interpret the forthcoming interface studies.

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Physical Chemistry **522**

Effect of salts and surfactants on the excited-state dynamics of organic dyes at liquid/liquid interfaces studied by femtosecond surface second harmonic generation technique

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The effect of salts and surfactants on the excited-state dynamics and adsorption of organic dye molecules at liquid/liquid interfaces was studied using time-resolved and stationary surface second harmonic generation (SHG) techniques.[1] Addition of salts or surfactants affects the adsorption of the organic dye molecules at the interface through Coulomb interactions.[2] In particular, the addition of anionic salts or surfactants significantly increases the adsorption of cationic malachite green (MG) dye at the interface and provokes the formation of MG aggregates. The aggregation phenomenon manifests itself in a dramatic change of the excited-state dynamics of MG (Fig. 1a) and leads to the red shift in its SHG interfacial spectrum (Fig. 1b).

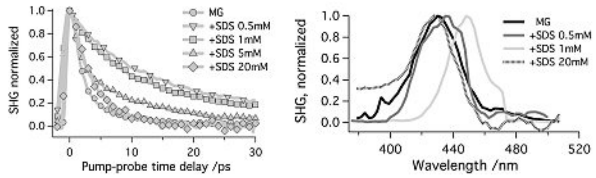

Fig. 1. Effect of the anionic SDS surfactant on the excited-state dynamics (a) and SHG interfacial spectrum (b) of the cationic MG dye.

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Physical Chemistry **523**

Excited-state dynamics of zwitterionic biaryls

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Nonlinear optical (NLO) materials are of high interest for applications in photonics and photoelectronics since their properties can be modified by intense light, in turn affecting the properties of the light itself. Biaryl push-pull molecules composed of a donor and an acceptor connected through a π-conjugated bridge are promising systems for NLO. [1] Betaine-30 (B30), the most famous compound of this class, undergoes intramolecular charge transfer upon photoexcitation resulting in a large decrease of electric dipole moment. Furthermore, it is nonfluorescent at room temperature due to ultrafast radiationless deactivation. We have investigated the excited-state dynamics of zwitterionic biaryls that consist of a phenolate donor connected to acceptors of varying strength. Femtosecond time-resolved fluorescence, visible and infrared transient absorption as well as *ab initio* calculations have been used to obtain a comprehensive picture of their photophysics. As the nonradiative decay of these compounds is associated with substantial structural changes, transient infrared spectroscopy is a powerful tool to study this process and provides precious information. The dynamics observed are compared to those that have been reported for closely related biaryl zwitterions, [2] and for B30. [3] Based on this work, we can obtain further insight into the relationship between chemical and optical properties of biaryl compounds.

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Physical Chemistry **524**

In-situ Investigation of Dye Adsorption on TiO_2 Films Using a Quartz Crystal Microbalance and Atomic Force Mircoscopy

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Dye sensitized solar cells (DSCs) are a viable alternative to silicon solar cells due to their low cost and relatively high efficiency [1]. The self-assembled monolayer of dye molecules on the TiO_2 photoanode plays a crucial role for light harvesting, and also acts as a blocking layer. To prevent recombination, coadsorbates have proven to be essential, but little is known on the interaction between the dye and different coadsorbates.
Herein, we employ a quartz crystal microbalance with dissipation technique (QCM-D) [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 an organic donor – π-bridge – acceptor dye (Y123) and a coadsorbate (Cheno). For the first time a molar ratio of the two species when coadsorbed on the surface is determined. In addition to precise quantification of dye loading, we study the adsorption / desorption kinetics on flat and mesoporous semiconductor films and demonstrate the immense potential of the latter for sensing applications. Finally, our results are complemented 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.

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Physical Chemistry **525**

Surface Enhanced 2D-IR spectroscopy of gold nanoparticle capping layers

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The plasmonic enhancement of an electric field around a spherical metal nanoparticle strongly perturbs the optical response of bound molecules in the visible part of the electromagnetic spectrum. Such surface field enhancements might be expected to play only a limited role in the infrared part of the spectrum. In this presentation however, we show that a Mie theory analysis of the electric field around a spherical gold nanoparticle illuminated at infrared wavelengths predicts that the near-field amplitude peaks at a value ~3 times larger than the incident field amplitude. Incorporating the effects of orientational averaging, we show that the infrared intensity enhancement Q_{IR} for a radially oriented dipole at the surface a metal nanoparticle is ~9. As 2D-IR spectroscopy is a third order nonlinear method, 2D-IR signals will be enhanced by up to a factor of Q_{IR}^2 (~81).

In order to characterise the predicted enhancement effects, we use 2D-IR spectroscopy to study aqueous gold nanoparticle suspensions (*d*=10-25 nm), where the nanoparticle capping layers comprise various kinds of thiols and peptides containing amide and carboxyl reporter groups. For 20 nm gold nanoparticles we observe a factor of 20x enhancement in 2D-IR signal size from an amide group near the gold surface. If the nanoparticles are aggregated, the enhancement increases to ~100x. Through changes in reporter distance, orientation, nanoparticle size and the state of nanoparticle aggregation, we confirm the infrared enhancement effect and gain a more detailed insight into the structure and dynamics of the nanoparticle capping layers compared with FT-IR spectroscopy.

Physical Chemistry **526**

2D IR Spectra of Cyanide in Water Investigated by Molecular Dynamics Simulations

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Ultrafast 2D IR vibrational spectroscopy can provide unique information related to the dynamics, interactions, and structures of molecular systems. Often the spectra from 2D IR experiments contain a convolution of various information, and the interpretation of the spectra can be facilitated by the aid of computer simulations. Frequency-frequency correlation functions (FFCFs) can be used as a bridge connecting experiment and computer simulations. The cyanide ion in water has been studied extensively by experiments [1-3] and is simple to model. Therefore, the computational modeling of the system would be appropriate to shed light on the relationship between the experiments and simulations. In this work, we demonstrate that with physically realistic force fields [4] 2D IR spectra can be computed which agree with experiment. In particular, the tilt angle $\alpha(t_2)$ in the 2D spectra as a function of the waiting time t_2 was determined from the simulations and compared with the experimental result [2]. It is shown that simulations with the best available interaction potentials yield $\alpha(t_2)$ very close to the experiment.

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Physical Chemistry **527**

Dynamics and vibrational spectroscopy of water at silica surface

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The interaction of silica (SiO_2) with water is of interest in understanding the solid-liquid interface. A number of experimental[1,2,3] and theoretical studies [4,5,6] have provided molecular level insights into the behavior of interfacial water. The structural and dynamical properties of the interfacial water can be significantly affected by the silica surface. In the present study, classical Molecular dynamics simulations are performed to investigate dynamical, structural and vibrational properties of water at the silica-water interface. We observe that water molecules are organized with high-density area between the surface hydroxyl group yielding a distinct pentagonal pattern. Data from the first atomic layer from the silica surface suggest a high prefential orientation with one OH group pointing towards the surface. The vibrational spectra of water molecules shows a new shoulder peak near the bending mode of water and is due to water molecules attached through hydrogen bonding to the silica -OH group[3]. This peak is also found in deuterated samples (HOD/D_2O), however the peak position and intensity are shifted, due to isotopic effects. Other analysis such as radial distribution function and the average cosine of the angle between water dipole vector and normal of the surface are also calculated.

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Physical Chemistry **528**

IR/UV-Depletion Spectroscopy of 2-Pyridone·$(NH_3)_n$ n=0-3 Clusters

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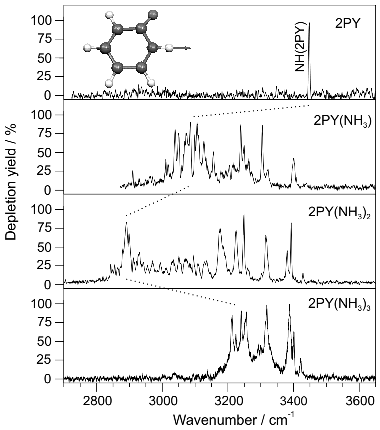
We measured mass-specific IR-depletion spectra of 2-pyridone·$(NH_3)_n$ clusters with n=1-3 to investigate the possibility of proton transfer in the ground state. This has been predicted to occur for n=5 [1]. The N-H stretch frequency of the 2-pyridone unit shifts to the red with n=0-2 [2]. For n=3 however, the band for the 2PY N-H stretch shifts back to the blue.



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Physical Chemistry **529**

Methyl Torsional Bands of the Jet-Cooled Adenine Analogue 9-Methyl-2-Aminopurine

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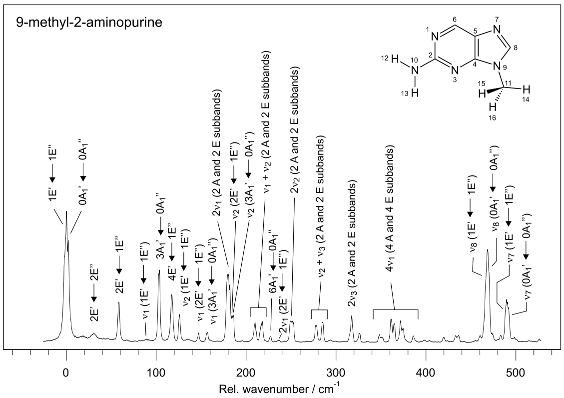
We have investigated the UV vibronic spectra and excited-state nonradiative processes of supersonic jet-cooled 9H-2-aminopurine (9H2AP) and its water clusters by two-color resonant two-photon ionization spectroscopy [1,2]. For 9-methyl-2-aminopurine (9M2AP) we found a ~100 ps S_1 state lifetime and rapid intersystem crossing to the T_1 ($^3\pi\pi^*$) state, similar to 9H2AP [1]. In the vibronic spectrum of 9M2AP coupling of methyl torsional motion to out-of-plane vibrations is observed. Thereby, transitions to fundamental out-of-plane vibrations that are normally forbidden appear in the spectrum.



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Physical Chemistry **530**

Supersonic Jet Spectroscopy of Weak Perylene-Based Charge-Transfer Complexes

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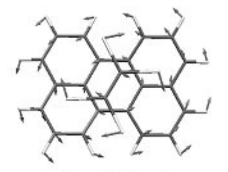
Charge-transfer (CT) complexes are characterised by an electronic transition to an excited state with partial transfer of electronic charge. They are of great interest in the development of new conductive materials and superconductors. Several CT complexes of perylene with chloroethylenes such as trans-1,2-dichloroethylene (DCE) and tetrachloroethylene (TCE) were investigated by resonant two-photon ionisation (R2PI) spectroscopy.


$R_c = 12.4\ cm^{-1}$
Perylene·Dichloroethylene


$R_c = 17.0\ cm^{1}$
Perylene·Tetrachloroetyhlene

The computational analysis shows that six intermolecular modes are newly generated upon complexation with either chloroethylene derivative. These six modes were grouped into three rotational (R_a, R_b, R_c) and three translational (T_x, T_y, T_z) modes [1]. These modes were assigned to prominent bands and progressions in either spectrum.

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Physical Chemistry **531**

In Situ ATR-IR Spectroscopy Investigation of Water at the BSA Protein - TiO_2 Interface

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It is of general interest to understand protein adsorption from an aqueous environment to a solid surface. In this work, we studied protein adsorption onto TiO_2 surfaces and its dependence on visible light irradiation. Furthermore, the releasing of adsorbed water from the surface upon protein adsorption is followed. Attenuated total reflection infrared (ATR-IR) spectroscopy using a flow-through cell is an important tool for investigating this crucial behavior. Adsorption of Bovine Serum Albumin (BSA) was performed in water at concentrations of 10^{-6} mol/L at room temperature. The curve fitting method of the second derivative spectra allowed us to explore details of the secondary structure of pure BSA in water and conformation changes during adsorption and illumination by visible light. The results clearly show that releasing water from the surface strongly depends on the concentration of adsorbed BSA. During visible light illumination the protein spreads on the surface thus displacing more water. This curious phenomenon of water release in between BSA and the TiO_2 surface is reversible because of the voids between adsorbed BSA molecules.

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Physical Chemistry **532**

Adsorption of chiral thiols on gold nanoparticles: An in situ ATR-IR study

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Attenuated total reflection infrared (ATR-IR) spectroscopy is used to study in situ the adsorption of gold nanoparticles (GNP) on a Ge ATR crystal and their chiral modification by 1, 1'-binaphthalene-2, 2'-dithiol (BNSH). For this work, the Ge ATR crystal is first functionalized using plasma cleaning and adsorption of the positively charged polyelectrolyte poly (allylamine hydrochloride). Then citrate-stabilized gold nanoparticles are adsorbed onto the modified Ge ATR crystal. When BNSH solution is flowed over the gold surface, BNSH is adsorbed by partial replacement of the citrate as evidenced by the ATR spectra (Figure 1). The BNSH molecules form a self-assembled monolayer (SAM) on that gold surface, which can discriminate between the enantiomers of phenylalanine.

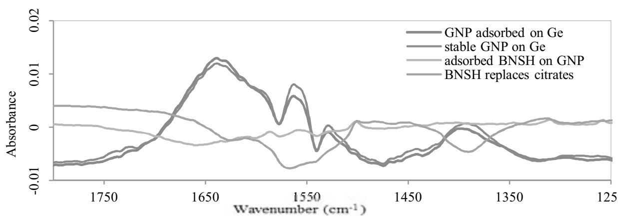

Figure 1. ATR-IR spectra of adsorbed GNP on Ge and adsorbed BNSH on GNP.

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Physical Chemistry **533**

Fluorescence Property of Unsymmetric Indolylmaleimide Derivatives

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We have focused on indolylmaleimide derivatives (IMs) as novel luminescent compounds. IMs have been developed for useful fluorescent probes and organic light-emitting diodes. In our previous study, various bisindolylmaleimides having fluorescence (FL) emission maxima wavelengths longer than 500 nm, large Stokes shifts longer than 200 nm and different FL emission wavelengths at excitation wavelength of 365 nm were developed [1]. Furthermore, the facile synthesis and FL properties of novel unsymmetric IMs were clarified [2]. However, there is no report on unsymmetric IMs having FL emission maxima wavelengths longer than 500 nm and high FL quantum yield. Thus, based on expanding the π–conjugation and the introduction of representative FL compounds, pyrene, biphenyl, bithiophene, and carbazole into a maleimide moiety in unsymmetric IMs were selected. The FL emission maxima wavelengths of these IMs were 562–597 nm in dimethylfomamide. The large Stokes shifts longer than 106 nm were observed. *Ab initio* quantum chemical calculation of 3-Bithiophene-4-(1*H*-indol-3-yl)-2,5-dihydro-1-methyl-2,5-pyrroledione suggested that the HOMO and LUMO were localized in the indole ring and maleimide moiety, respectively. The localized molecular orbitals initiate the intra-molecular charge transfer process. These results provide significant information for rational design of the unsymmetric IMs as fluorescent probes.

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Physical Chemistry **534**

Examination of DSCs using scanning electrochemical microscopy

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We present initial studies into the electronic surface effects observed using scanning electrochemical microscopy on dye-sensitized solar cells (DSCs).

The use of scanning electrochemical microscopy (SECM) as a tool to examine local electrochemical behavior in the solid state is becoming more common in modern material science.[1] Recent research within our group has focused upon the development of a number of novel dyes and electrolytic systems with potential applications in dye sensitized solar cells.[2] In order to better understand the processes resulting from changes in the dyes used and the electrolytic system present in the cell, SECM techniques have been applied in order to examine the electrochemical processes occurring. Comparison of the surface currents observed for both bare fluorine doped tin oxide (FTO) and FTO layered with dye coated titanium dioxide, gives information about both the solar cell topology and efficiency.

The surface activities of DSSC's have been examined for a series of electrolytes, using the commercially available ruthenium N719 dye absorbed on titanium dioxide. Studies into the effect of application of light to the DSSC setup and the resulting changes, both in the current-voltage curve response and the charges induced by both electron transfer and hole injection at the surface of the cells have also been carried out.

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Physical Chemistry **535**

Broadband homodecoupling in the indirect dimension of 2D homonuclear NMR experiments

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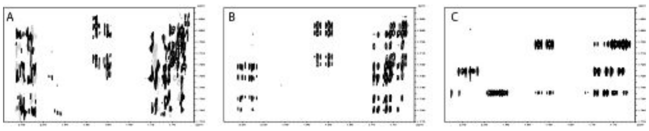
The coupling structures in proton spectra often cause signal overlap making it difficult to exploit one- and two-dimensional spectra such as COSY, TOCSY, etc. The simplification of the multiplets in the indirect F1 dimension into singlets can be obtained using the homonuclear decoupling scheme developed by Zangger-Sterk [1].

We modified that spatial encoding element and implemented it in the TOCSY experiment [2]. When recorded with a sufficiently large number of increments, or in combination with spectral aliasing, the resulting spectra completely resolve the signals of protons only a few Hertz apart.



Comparison of the TOCSY spectra of 4-Androstene-3,17-dione. (A) Classical TOCSY, (B) TOCSY with zero-quantum elimination, (C) TOCSY with homonuclear decoupling and zero-quantum elimination.

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Physical Chemistry **536**

Measurements of ^{13}C-^{13}C coupling constants using selective refocusing within the BBHD-HSQC sequence

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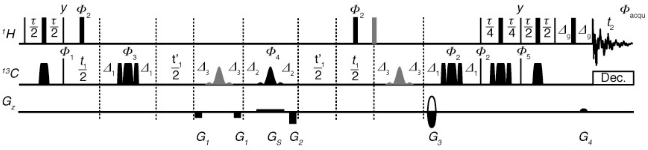
Scalar coupling constants can give insights about the structures of molecules but they also cause complex signal multiplicities which reduces the sensitivity of the experiments and often results to extensive signal overlap. We recently introduced a BBHD-HSQC [1] sequence to eliminates the effect of ^{13}C-^{13}C scalar couping constants in the indirect dimension [2] of the HSQC spectra of ^{13}C-enriched compounds.

In order to be able to measure selected ^{13}C-^{13}C coupling contants, a selective refocusing pulse can be included into the BBHD sequence. Two versions are presented in which the coupling constants of the selected carbon with all its coupling partners are either measured in the split of signals in the indirect dimension or determined by comparison of the signal intensities in a pair of complementary spectra.



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Physical Chemistry **537**

Morphological Characterization of Novel Self-Assembled of Biopolymer-Oligonucleotide Hybrids

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The self-assembly of amphiphiles is a well-known phenomenon and numerous structures have been observed and systematically studied in the solid state, at the air-water interface, and in aqueous solution as reported in several publications. One excellent example along this direction is the investigation of the structure formation of poly(1,2-butadiene)-block-poly(ethylene oxide) diblock copolymers (PB-b-PEO) crystals [1], films spread at air-water interface [2], and micelles self-assembled in aqueous solution [3]. We are particularly focusing on the coupling between a DNA fragment (ssDNA) and suitable biocompatible polymers to achieve self-assembling biocompatible copolymers. Our recent results on the morphological characterization of newly synthesized self-assembling biopolymer-oligonucleotide hybrids through surface characterization techniques such as Atomic Force Microscopy (AFM) will be presented. Investigations in different solvent systems, at various pH, temperatures and ionic strengths are carried out to elucidate the role of intra- and intermolecular interactions (e.g. hydrogen bonding) on the structure formation and modes of interactions of the self-assembled biopolymer-oligonucleotide hybrids to eventually achieve a comprehensive understanding of the self-assembly mechanism of these novel copolymers.

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Physical Chemistry **538**

Static and dynamic properties of a strong-leg spin ladder

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Infinite-size spin systems are of current interest both in solid state physics as well as numerical and theoretical physics. Of special interest are one-dimensional spin systems in chain or ladder arrangement. Such spin systems are naturally realized in *e.g.* organometallic crystals where large organic molecules separate copper-halogen complexes interacting with each other via Cu-X-X-Cu (X=Cl, Br) superexchange pathways. We investigated the spectral and dynamic properties of Bis (2,3-dimethylpyridinium) Tetrabromocuprate (Dimpy). Dimpy is a clean and symmetric $S = 1/2$ spin-ladder material in the rare strong-leg coupling regime ($J_\mathrm{l} > J_\mathrm{r}$), described by the Hamilton operator

$$\hat{H} = \sum_{n=-\infty}^{\infty} J_\mathrm{l}\,(\hat{\mathbf{S}}_n^{(1)}\hat{\mathbf{S}}_{n+1}^{(1)} + \hat{\mathbf{S}}_n^{(2)}\hat{\mathbf{S}}_{n+1}^{(2)}) + J_\mathrm{r}\,\hat{\mathbf{S}}_n^{(1)}\hat{\mathbf{S}}_n^{(2)}. \qquad (1)$$

In our laboratory, large deuterated single crystals were grown according to the temperature gradient method. We measured heat capacity and magnetization at low temperatures (down to 50 mK) and high magnetic fields (up to 14 T) demonstrating *e.g.* the quantum phase transition from the spin liquid to Luttinger spin liquid state. The excitation spectrum was studied in zero and applied magnetic fields with inelastic neutron scattering experiments, with both the triple-axis and the time-of-flight technique. All measurements are in spectacular agreement with state-of-the-art numerical DMRG calculations.

Physical Chemistry **539**

Exploiting the space-charge effects for measuring the number of ions trapped in a FT-ICR mass spectrometer.

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Fourier transform ion cyclotron resonance mass-spectrometry (FT-ICR MS) has become a popular method for high resolution analysis of high molecular weight compounds such as peptide and/or proteins. In addition to qualitative identification of the proteins present in a sample, quantification allows one to determine concentrations of proteins in a sample, and to investigate reaction rates and reaction equilibria. FT-ICR MS has been often utilized for the quantitative analysis. However, the accuracy of FT-ICR MS-based approach for ion quantification needs to be evaluated, especially for complex samples. In this work, we experimentally evaluate the possibility of utilizing the space charge effect from trapped ions on the observed FT-ICR signal for quantitative assessment of the number of confined ions.

Experiments were performed using two FT-ICR mass spectrometers: commercial 4.7 T system and a home-built hybrid 1.25 T FT-ICR mass spectrometer. In this work, we present the results for determining the number of ions by three independent methods: (i) observing of peak coalescence, a direct result of space-charge effects[1], (ii) evaluating the deviation of the magnetron frequency from its theoretical value[2], and (iii) direct measuring of the voltage signal generated by the orbiting ions on the detection electrodes of the FT-ICR ion trap[3].

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Physical Chemistry **540**

Cetylpyridinium Peroxydisulfate (CPPS) as an Individual Substance

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We have performed systematically investigation of synthesis of quaternary ammonium salts (QAS) of peroxydisulfonic acids and physicochemical properties of cetylpyridinium peroxydisulfate (CPPS) as an individual substance. The aim of this article to investigate the specificities and physicochemical properties of CPPS, which will help both to expand the scope of applicability of such substances and to understand the mechanism of their participation in the different chemical processes. The new substances have been obtained by interaction of QAS with potassium peroxydisulfate (PPS) in aqueous media [1,2]. The separation of new substances from aqueous media is depended on length of carbon chain of QAS molecule or their hydrophobic-hydrophilic balance. Molecules of these substances contain two functional groups allowing them to play dual role: both initiator-catalyst of chemical processes and stabilizer for two-phase system. Our present efforts are concentrated on the establishment of CPPS application in polymerization reactions.

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Physical Chemistry **541**

Photoinduced processes in pristine cyanine thin films and fullerene bilayers for organic photovoltaics

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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, which is responsible for higher charge carrier mobility.[1] Small molecules such as cyanine dyes are potential candidates as electron donors due to their high extinction coefficient which enables the use of thin active layers and therefore enhances charge separation at the donor/acceptor interface.

Lately, 2% efficiency has been reported by Fan *et al* for doped cyanine dyes as donor material and fullerene C_{60} as electron acceptor.[2] Actually, a long exciton diffusion length in cyanine/C_{60} bilayer heterojunction is stated as a conclusive explanation for the unexpected large IPCE value in 30 nm thick cyanine films. Work from Castro *et al*. state a near unit charge transfer quantum yield for cyanine/MEH-PPV solar cells, which suggest a different picture of charge generation than the Frenkel exciton model.[3]

The photoinduced processes occurring in pristine and bilayer thin films are investigated via femtosecond transient absorption spectroscopy and nanosecond flash photolysis in order to determine the first steps of charge separation and recombination. The pristine cyanine thin film exhibit charge separated states living up to the microsecond time scale, and the mechanism of formation of those states is currently addressed.

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Physical Chemistry **542**

Towards merged-beam experiments of neutral particles

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Collision experiments with fast beams can be performed at low collision energies if the beams move parallel in the same direction. Compared with crossed beam setups this leads to enhanced interaction volumes which make the detection of smaller cross sections possible.

In order to completely overlap the two beams and to assure their parallel movement, a high level of control over the motion of the particles is mandatory. So far, this could only done when at least one of the beams consists of charged particles. Progress in using the Stark and Zeeman effect to manipulate neutral particles have now reached a level where merged-beam experiments for neutral-neutral collisions become possible.

We are presently constructing a setup where two guides, one electric and one magnetic, for fast particles from supersonic expansions are merged which will enable the study of a very wide range of collision systems between polar and paramagnetic particles in a range of relative velocities between zero and several 100 m/s.

This planned setup will be presented as well as our approaches to extract the maximum information from such an experiment.

Physical Chemistry **543**

Probing the Catalytic Cycle of Cytochrome P450 for Reaction Intermediates

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Cytochrome P450 (CYP) enzymes are heme-containing mono-oxygenases that catalyze a wide variety of oxidation reactions, including stereo- and regioselective hydroxylation of non-activated C–H bonds.[1] Although CYPs have been studied for over 40 years, controversy regarding the catalytic mechanism continues. In analogy to the "compound I" of peroxidases, an oxido-iron(IV) π-cation radical intermediate is generally thought to be the most oxidizing species in the CYP reaction cycle.[2] However, this intermediate has never been convincingly detected.

The aim of this work is to elucidate unresolved issues in the catalytic cycle of the camphor-hydroxylating soluble cytochrome P450 isozyme, (P450cam, CYP101) from the soil bacterium *Pseudomonas putida*. We used CW-EPR spectroscopy to characterize recombinant CYP101 produced in high yield (57mg/500mL culture) and purity ($A^{395}/A^{280} = 1.63$) in *Escherichia coli* BL21 cells. By pulse radiolysis, a time-resolved rapid kinetics method, we detected a transient species with an absorbance maximum of 690 nm, consistent with compound I. We have applied pulsed-EPR spectroscopy to detect and characterize intermediates from reaction of CYP101 with peracids after irradiation and accumulation at ultra-low temperatures.

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Physical Chemistry **544**

Initial-value representation for the Fidelity

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We obtain an initial value representation for the quantum Fidelity from the semiclassical theory of Wigner function evolution, together with the classical first-order perturbation theory. In the limit of small actions, the amplitude of each trajectory reduces to unity, just as in the *dephasing representation* introduced by Vaníček in Ref. [1], but these trajectories are generated here by the mean Hamiltonian for both the forward and the backward motion. This slight change of action may substantially alter the phase. The amplitude correction depends on the second derivative of the action. This improved dephasing approximation is verified to work even for quadratic Hamiltonians, for which the semiclassical evolution is exact, thus extending the range of application beyond its original scope in quantum chaos.

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Physical Chemistry **545**

Absolute cross-sections for dissociative electron attachment to $Pt(PF_3)_4$

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The study of $Pt(PF_3)_4$ was motivated by new applications of metal-organic compounds, which are used as precursors in Focused Electron Beam Induced Processing, to produce nano-size devices [1]. $Pt(PF_3)_4$ is a volatile compound which, in contrast to complexes with carbon-containing ligands, yields carbon free deposits [2].

We carried out a study of dissociative electron attachment (DEA) to $Pt(PF_3)_4$. The absolute cross sections were measured with a recently constructed TOF/TEM apparatus [3]. Absolute differential cross sections (CS) for elastic scattering, and for vibrational and electronic excitation of $Pt(PF_3)_4$ were measured [4]. Several anionic fragments resulting from DEA to $Pt(PF_3)_4$ have been observed: F^-, $Pt(PF_3)^-$, $PtPF_4^-$, $Pt(PF_3)_2^-$, $Pt(PF_3)_3^-$ and even Pt^- (with a low cross section of 1.77 pm^2) [5]. The corresponding DEA spectra reveal two low-lying resonances at 0.52 and 1.8 eV as well as three higher-lying resonances at 5.8 eV, 6.8 eV and 12.0 eV, respectively, which are in good agreement with the observations made by means of resonant vibrational excitation and electronically excited states characterized by electron energy-loss spectra [4]. The two lower bands are assigned to shape resonances, the three higher-lying bands to Feshbach resonances with Rydberg parent states [4]. We found $Pt(PF_3)_3^-$ to be the by far dominant fragment formed in electron attachment to $Pt(PF_3)_4$ at low energies (< 2 eV), with a CS of 20'000 pm^2.

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Physical Chemistry **546**

Probing the Silica-Aqueous Interface with In Situ XPS and XAS

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We have recently extended in situ XPS[1] and XAS[2] to the silica (SiO_2) nanoparticle-aqueous interface using a liquid microjet in combination with synchrotron radiation. Our in situ XPS[1] measurements of 7 nm SiO_2 at pH 10 show two distinct electronic structures in the Si 2p region at 107.8 and 106.5 eV. Electron kinetic energy dependent measurements allow the two components to be assigned to the bulk of the nanoparticle, and to the surface of the nanoparticle that is in direct contact with solution, respectively. Our in situ XAS[2] measurements at the Si K-edge as a function of pH for nanoparticles of 7, 12, and 22 nm reveal a change in shape of the Si 1s – t_2 absorption brought about by changes in solution pH. Our results are consistent with the number of silanol groups changing protonation state being inversely correlated with SiO_2 nanoparticle size. The importance of in situ studies will also be discussed by comparing the XAS spectra of aqueous 7 nm SiO_2 with the same dehydrated sample in vacuum.

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Physical Chemistry **547**

Ultrafast time-resolved photoelectron spectroscopy of solvated species

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We are currently developing an ultrafast pump-probe experiment to study electronically excited states and electron dynamics in solution. Combining photoelectron spectroscopy with the liquid microjet and an attosecond interferometer will allow us to map the temporal evolution of occupied orbitals in solvated species upon photoexcitation [1, 2]. This opens the path towards real-time monitoring of ultrafast processes under ambient conditions.

Our high-harmonic radiation source produces trains of attosecond pulses using a femtosecond 800 nm pulse. An innovative actively stabilized attosecond interferometer controls the time delay (50 as to 300 fs) between these pulses, selects one particular high harmonic energy (XUV probe pulse) and frequency-doubles the 800 nm radiation (UV pump pulse). Photoelectrons emitted from the liquid jet are collected and energy analyzed by a magnetic bottle spectrometer. Information on the orbital binding energy and population of electronic states is extracted from the time of flight of the photoelectrons and the corresponding signal intensity.

The experiments of interest range from proton transfers in photoacids, over charge-transfer processes in transition metal complexes and band gap excitations in nanoparticles, to chemical reactions and biological systems. The results of our experiment are expected to have important implications for the understanding and tailoring of the electronic structure and dynamics of nanoscale systems that have found a wide range of scientific and technological applications in photochemistry, solar cells and heterogeneous catalysis.

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Physical Chemistry **548**

Versatile velocity-map-imaging spectrometer for strong-field and attosecond experiments

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Velocity-map imaging (VMI) of photoelectrons is a powerful, yet experimentally simple tool to obtain information on the electronic structure of molecules. The recent development of new attosecond and strong-field light sources calls for the development of specialized detectors that will allow their potential to be fully exploited. Current VMI spectrometers follow two main designs, the first, traditional design being optimized for optimal rotational and vibrational cooling of the molecules and the second being optimized for high particle densities. We present an innovative velocity-map-imaging spectrometer that allows a continuous tuning of the particle density and the sample temperature. This new design allows us to optimize the experimental conditions for a range of experiments using intense infrared laser pulses and/or attosecond pulses. We will use laser-induced electron tunneling and rescattering for probing nuclear rearrangements in photochemical reactions and imaging proton dynamic on an attosecond timescale. With techniques of impulsive alignment and orientation, molecules will be fixed in space. As a result, the laser-driven electron rescattering process can be measured in the molecular frame, providing detailed insights into the geometric and electronic dynamics of molecules.

Physical Chemistry **549**

Actively Stabilized Attosecond Interferometer

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Attoseconds (10^{-18} s) are the natural time scale on which electronic motion takes place in the valence shell of molecules. Insights about electronic dynamics and the structure of polyatomic molecules on this timescale are expected to lead to a deeper understanding of electron correlation, which determines the shape and reactivity of all molecules. We report the design and construction of an interferometer, that generates a controlled attosecond delay between two ultrashort infrared or ultraviolet and extreme ultraviolet pulses and represents a versatile tool to realize pump-probe measurements on the attosecond time scale. The innovative setup will be combined with a currently operating velocity-map-imaging (VMI) spectrometer or, alternatively, a photoelectron time-of-flight spectrometer for liquid samples. Molecular systems of chemical relevance will be studied. To reach long-term stability of the pulse delay with accuracy in the attosecond range, the delay line has to be actively stabilized. Using a simple laser interferometer in parallel to the main beam paths would give a repetitive signal for each half-wavelength and its sinusoidal signal shape would not allow stabilizing to each position with the same feedback parameters. Therefore we are using a sophisticated stabilization scheme, modulating the path length of the stabilization interferometer and detecting its phase, to be able to stabilize to arbitrary positions. The feedback loop is realized fully digitally in a real-time computer system and the path length is adjusted by a long range piezo stage and a fast piezo mirror, which allows loop rates in the kilohertz range with absolute delays from 0 to about 1 ps. In addition, a white-light interferometer gives information about the absolute path-length difference between the two interfering beams. With those two independent control mechanisms it is always possible to keep a well-defined delay over long timescales and perform stable and reproducible pump-probe measurements.

Physical Chemistry **550**

High-harmonic spectroscopy of isoelectronic molecules: electronic structure and multielectron effects

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High-harmonic spectra of transiently aligned molecules are a sensitive probe of the electronic structure and dynamics of molecules. Furthermore, they enable the access to the attosecond electron dynamics in molecules. A pronounced minimum in the spectrum of aligned CO_2 molecules has been previously assigned to structure, dynamics, or the interplay of both. We combine high harmonic spectroscopy with theoretical modeling of aligned CO_2 and the isoelectronic molecule, N_2O, to understand which of these interpretations is most appropriate. We find that the position of the spectral minimum differs significantly in the two molecules. Although the overall length of the two molecules is almost identical, the nodal plane in the highest-occupied molecular orbital (HOMO) of N_2O is displaced towards the O-atom compared to CO_2. The comparison of our experiments and calculations shows that the difference in the observed position of the minima is directly related to the location of the nodal plane of the HOMO of the molecules. This study therefore shows the relation of the high-harmonic spectra of molecules to their electronic structure.

Physical Chemistry **551**

The ground $\mathrm{X}^+\ {}^2\Pi_\mathrm{g}$ and first excited $\mathrm{A}^+\ {}^2\Pi_\mathrm{u}$ electronic states of Cl_2^+ studied by high-resolution PFI-ZEKE photoelectron spectroscopy

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Partially rotationally resolved pulsed-field-ionization zero-kinetic-energy (PFI-ZEKE) photoelectron spectra of the $\mathrm{X}^+\ {}^2\Pi_{\mathrm{g},\Omega} \leftarrow \mathrm{X}\ {}^1\Sigma_\mathrm{g}^+$ $(\Omega = 3/2,\ 1/2)$ photoionizing transition of Cl_2 have been recorded. Spectra of all three isotopomers (${}^{35}Cl_2^+$, ${}^{35}Cl{}^{37}Cl^+$ and ${}^{37}Cl_2^+$) could be measured in the region of $v^+ = 0 - 5$ and $v^+ = 25 - 40$, corresponding to the wavenumber ranges $92\,500 - 96\,500\ \mathrm{cm}^{-1}$ and $106\,750 - 115\,500\ \mathrm{cm}^{-1}$. The analysis of the rotational structure and the isotopic shifts of these spectra has enabled the derivation of an improved value of the first adiabatic ionization energy ($92\,647.7 \pm 0.3\ \mathrm{cm}^{-1}$ for ${}^{35}Cl_2$). In combination with other data [1,2], new values for the dissociation energies D_0 of Cl_2 and Cl_2^+ could also be derived ($19\,997.4 \pm 1.1\ \mathrm{cm}^{-1}$ for ${}^{35}Cl_2$ and $31\,940.7 \pm 1.1\ \mathrm{cm}^{-1}$ for ${}^{35}Cl_2^+$). The potential energy function of the X^+ state of Cl_2^+ was determined in a least-squares-fitting procedure. In addition, several low-lying vibrational levels of the upper spin-orbit component of the $\mathrm{A}^+\ {}^2\Pi_{\mathrm{u},i}$ state could be assigned for the first time [3,4,5]. The PFI-ZEKE photoelectron spectra also contain a series of as yet unassigned lines and reveal numerous perturbations.

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Physical Chemistry **552**

High resolution spectroscopy of ultracold Rydberg atoms

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The study of dense samples of ultracold atoms in high Rydberg states has yielded many spectacular results in recent years, such as the observation of exotic dimers with bond-lengths exceeding 1 μm [1]. We present new high-resolution spectroscopic experiments on Rydberg states of Cs at temperatures around 100 μK. Laser-cooled Cs atoms are excited from the $6S_{1/2}$ state to Rydberg states by a UV photon. A phase-locked narrowband source of continuous millimeter waves (linewidth <1 kHz) is then used to determine Rydberg-Rydberg transition energies with highest accuracy. Rydberg atoms are detected state-selectively by field-ionization. Line broadening by stray electric and magnetic fields and from interactions between Cs atoms is investigated.

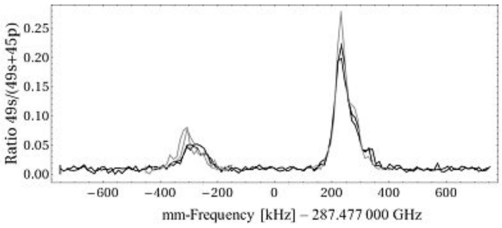

Fig. 1: Transfer of population from $45P_{3/2}$ state of cesium to the $49S_{1/2}$ state by mm-wave radiation. The two main features correspond to the hyperfine structure of the $49S_{1/2}$ state broadened by the unresolved hyperfine structure of the $45P_{3/2}$ state. A fit of a model spectrum to the data yields an line width of 38 kHz, close to the transform limit of the 30 μs transfer pulse. Light and dark lines are taken at different magnetic fields.

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Physical Chemistry **553**

High-Resolution, Mass-Selective Spectroscopy in a Supersonic Jet Between 1-14 Terahertz: Rydberg Spectroscopy of Xe Atom

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An experimental apparatus has been developed that allows for high-resolution (down to $\sim 3\,\text{MHz}$), mass-selective spectroscopic investigations in a supersonic jet in the region between 0.1-14 terahertz (THz). It is based on the Fourier-transform limited, pulsed source of tunable THz radiation reported in [1].

To illustrate the properties of this new experimental apparatus, we report here Rydberg spectra of Xe in the region of 1-14 THz. Rydberg states of principal quantum number $n \sim 20$ have been prepared by irradiation of an atomic beam of Xe with vacuum ultraviolet (VUV) radiation. The narrowband, pulsed THz source was then used to record spectra of transitions from these Rydberg states to higher-lying Rydberg states. By increasing the length of the THz pulses, the spectral resolution could be adjusted betwen $\sim 3\,\text{MHz}$ and $\sim 100\,\text{MHz}$. The transitions were detected by selective field ionization and recording either the electrons or the ions, the latter offering the advantage of mass selection.

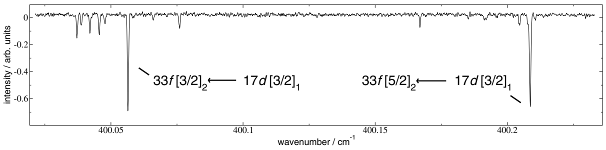

Figure 1: Rydberg spectrum of $33f \leftarrow 17d$ transitions of Xe at ~12 THz. The main transitions (see label) correspond to $I = 0$ isotopes. The weaker ones to ^{129}Xe ($I = 1/2$) and ^{131}Xe ($I = 3/2$).

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Physical Chemistry **554**

The Renner-Teller effect and the spin-orbit coupling in the ground state of the iodoacetylene radical cation (HC_2I^+)

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The $X^+\ {}^2\Pi \leftarrow X\ {}^1\Sigma^+$ photoionizing transition of iodoacetylene (HC_2I) has been investigated by pulsed-field-ionization zero-kinetic-energy (PFI-ZEKE) photoelectron spectroscopy. The first ionization threshold of HC_2I arises from the ejection of an electron from one of the p_{xy} lone pairs of the iodine atom. This results in a strong spin-orbit coupling in the $X^+\ {}^2\Pi$ ground state of HC_2I which is also subject to the Renner-Teller effect.

The combination of a narrow-bandwidth vacuum-ultraviolet (VUV) laser system [1] with optimized electric-field pulse sequences [2] enabled the resolution of the rotational structure of the PFI-ZEKE photoelectron spectrum of HC_2I in the region of the spin-vibronic ground state and of the fundamental of the bending mode ν_5 of HC_2I^+. The analysis provided accurate information on the structure of HC_2I^+, the photoionization dynamics of HC_2I and the Renner-Teller effect in ν_5. The current status of the analysis of the $X^+\ {}^2\Pi_{3/2}(v = 0) \leftarrow X\ {}^1\Sigma^+(v = 0)$ and $X^+\ {}^2\Pi_{3/2}(v_5 = 1) \leftarrow X\ {}^1\Sigma^+(v = 0)$ bands will be presented.

The Renner-Teller effect in the ground state of HC_2I^+ represents an example of the limiting case where the spin-orbit splitting is much larger than the vibrational intervals. Under these conditions, the Renner-Teller effect is quenched and only observable through weak forbidden vibrational bands.

The adiabatic ionization energy, the spin-orbit splitting of the electronic ground state and the ν_5 fundamental vibrational spacing have been determined to be 78296.3(2) cm^{-1}, 3257(2) cm^{-1} and 234(1) cm^{-1} respectively.

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Physical Chemistry **555**

DECAY PROCESSES IN COLD TRAPPED SAMPLES OF MOLECULAR HYDROGEN PREPARED BY RYDBERG-STARK DECELERATION

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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 two- and three-dimensional traps [2,3] for Rydberg atoms and molecules [4,5]. These experiments make use of the very large electric dipole moments associated with Rydberg Stark states.

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 molecules and collisions with the background gas [6]. In molecular Rydberg states, predissociation also contributes to the trap losses, and the ability to trap the Rydberg molecules enables one to study slow predissociation over several milliseconds. To quantify trap loss processes other than blackbody-radiation-induced transitions, an experimental setup which can be operated at 11 K has been developed. At these temperatures, the radiative decay of H Rydberg atoms and the slow predissociation of H_2 Rydberg molecules were investigated on the timescale of several milliseconds.

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Physical Chemistry **556**

Surface-based decelerators for Rydberg atoms and molecules

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A new generation of surface-based Rydberg-Stark decelerator will be presented. These devices rely on the large electric dipole moments (~ 1000 Debye) associated with Rydberg states of high principal quantum number. The forces exerted on samples in these states in the presence of inhomogeneous electric fields permit control of their translational motion. Experiments in which samples in pulsed supersonic beams have been accelerated, decelerated and electrostatically trapped using these devices will be presented. Rydberg H atoms moving with initial velocities of $\sim 700\ \text{ms}^{-1}$ have been decelerated to zero-velocity in the laboratory-fixed frame of reference within distances of 3 mm and times of $\sim 15\ \mu\text{s}$ [1]. The development of surface-electrode decelerators represents an extension of previous work on deceleration [2] and electrostatic trapping of Rydberg atoms [3] and molecules [4] using three-dimensional electrode structures. The general design of the surface-electrode decelerator is similar to that developed by Meek *et al.* [5] for deceleration of ground-state polar molecules, but modified and optimised for the deceleration of beams of Rydberg atoms and molecules. Such devices are of relevance to studies of Rydberg atom/molecule–surface interactions and applications in quantum information processing.

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Physical Chemistry **557**

Analysis of the highly resolved spectrum of CHD_2I in the region around 1000 cm^{-1} and the search for Intramolecular Vibrational energy Redistribution (IVR)

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We use methyliodide isotopomers ($CH_nD_{3-n}I$) as prototypes for the investigation of IVR with two different but complementary approaches [1]. The time-resolved approach based on 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 [2]. On the other hand, the frequency-resolved approach which will be discussed here uses the analysis of highly-resolved FTIR spectra to determine the coupling schemes between the vibrational states. This makes it possible to build an effective and sometimes the real molecular Hamiltonian, which by use of time-dependent quantum dynamics can derive the observed relaxation times independently [1,3]. Spectroscopic work at modest resolution has highlighted the strong coupling between the CH-stretching and bending modes, which may be related to the fastest relaxation times observed experimentally [3,4]. Here we present the analysis of the region around 1000 cm^{-1} of CHD_2I in order to investigate the couplings between the CD- or CH-bending mode (ν_4 or ν_3) and the combination and overtone bands in this region that include the low-frequency CI-modes. These couplings may be seen in relation with some of the slowest processes observed with the time-resolved approach.

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Physical Chemistry **558**

High resolution spectroscopy and vibrational dynamics of methane $^{12}CH_4$ and $^{13}CH_4$ up to 12000 cm^{-1}

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The present work is part of a larger study of a systematic analysis of the spectra of methane isotopomers [1, 2] in relation to the potential hypersurface of methane [3]. We report infrared spectra of $^{12}CH_4$ and $^{13}CH_4$ in the range 6500 to 12000 cm^{-1} measured with the Zurich interferometer Bruker IFS 125 prototype (ZP 2001) at 80 K in a collisional-cooling cell with optical paths ranging from 5 to 10 m. A preliminary analysis for both isotopic species was carried out and 13 new band centers were obtained for $^{12}CH_4$ as well as 8 new centers for $^{13}CH_4$ with an accuracy of 0.0001 - 0.0003 cm^{-1} from the direct experimental transitions. The 13 new band centers were added to 82 previously known band centers of the $^{12}CH_4$ molecule and a set of 26 vibrational, tetrahedral splitting, and resonance parameters was obtained from the fit of all 95 values of band centers. The set of parameters obtained reproduces the band centers with a root mean square deviation of about 1 cm^{-1}. In the analysis symmetrized vibrational functions have been constructed in the formalism of "irreducible tensorial sets", deriving equations which describe tetrahedral splitting of the states with $N \le 4$. On that basis, band centers of all vibrational states that correspond to $N \le 4$ (practically, up to 12000 cm^{-1}) have been estimated. Comparison of the known experimental band centers of $^{13}CH_4$ with the values of band centers predicted with the isotopic relations showed good agreement. In the final step the results obtained with the isotopic relations were used to find new bands for $^{13}CH_4$ in the region between 6500 and 12000 cm^{-1}, determined with high accuracy from the assignment of the experimental P(1) line in the cold spectra.

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Physical Chemistry **559**

A high resolution FTIR spectroscopic study of collisional-cooled CHF_3: Reanalysis of the strongly coupled states ν_2 and ν_5

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The infrared spectrum of CHF_3 is a prototypical spectrum of a classical symmetric top molecule. Despite a long history [1-7] its rotationally resolved infrared spectrum is poorly understood due to numerous strong interactions. For that reason we have started to reinvestigate the IR spectrum of CHF_3. In this paper we present an analysis of the strongly coupled triad states ν_2 and ν_5 previously measured and analyzed using FTIR supersonic jet spectroscopy [5]. The high resolution FTIR spectrum of CHF_3 has been measured with the Bruker 125 HR spectrometer using a collisional cooling cell [8] in the regions 1000-3600 and 5800-6800 cm^{-1} at two different temperatures, 120 and 295 K. In our present analysis we start by theoretical estimates of various parameters on the basis of a known *ab initio* intramolecular potential function [7]. The equations, which connect the most important interaction parameters with the parameters of the potential function, have been derived on the basis of operator perturbation theory. This information was used in the fit of experimental upper energy levels obtained from the assignment of transitions in the experimental spectrum. Interactions with further levels in the energy range will be discussed.

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Physical Chemistry **560**

Torsional-tunneling dynamics in aromatic compounds probed by synchrotron-based high resolution FTIR spectroscopy

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The understanding of the dynamic behavior of functional groups like the hydroxyl (OH) [1], the amino (NH_2) [2] or the aldehyde (CHO) group in biomolecules is essential for a complete understanding of their biochemical processes. In particular, tunneling processes which are generally neglected in classical biomolecular dynamics modeling are in fact important and deserve study. For that reason we have investigated the torsional tunneling dynamics of phenol (C_6H_5OH), aniline ($C_6H_5NH_2$) and benzaldehyde (C_6H_5CHO) as benchmark molecules using high resolution ($\Delta\nu$ = 20 MHz) FTIR spectroscopy [3] with synchrotron radiation [4]. We were able to detect tunneling processes for phenol and aniline in the spectral range from 7 to 30 THz (210-900 cm^{-1}) and for benzaldehyde between 25 and 30 THz. The tunneling dynamics take place on a time scale on the order of 20 ns to 350 ps depending on the excitation of various vibrational modes. We have probed the torsional tunneling dynamics of phenol in the first torsional excited state and upon excitation of other OH modes and detect large changes of the tunneling time up to a factor of 40. The torsional dynamics in aniline is complicated due to the inversion dynamics which have already been analysed decades ago [5]. We have identified the two torsional components rovibrationally resolved due to inversion splitting in the torsional fundamental of aniline and have detected within each inversion-torsional component two bands. In any case, the torsional tunneling splitting of the NH_2-group in aniline is much smaller than the torsional tunneling splitting of the OH-group in phenol. For benzaldehyde we detect torsional tunneling times upon excitation of in-plane-modes (600 to 1000 cm^{-1}) in the ns range.

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Physical Chemistry **561**

Inversion tunneling and stereomutation in chiral C_6H_4FNHD and C_6F_5NHD from infrared spectroscopy and quasiadiabatic channel reaction path Hamiltonian calculations.

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The inversion of the NH_2 group in aniline over the plane of the phenyl ring is a prototypical example of tunneling dynamics. An early determination led to a barrier for the tunneling process of about 450 cm^{-1} [1]. The tunneling process through the barrier splits the ground state and also many vibrationally excited states into two tunneling components. We have previously studied tunneling by ISOS spectroscopy of aniline and aniline(NHD) in a supersonic jet demonstrating the inhibiting nature of the NH-stretching mode [2,3,4,5]. Here we report the spectra and assignments of the NH-stretching states up to the second overtone in the room temperature FTIR spectra of ortho-C_6H_4FNHD and C_6F_5NHD as well as the direct measurement of ground state tunneling splittings in both molecules. We report also theoretical calculations where the dependence of the stereomutation process upon the excitation of other vibrational modes was approximately treated on the basis of DFT calculations with B3LYP/6-31G** using the quasiadiabatic channel reaction path Hamiltonian (RPH) [5,6] and shows a strong mode selectivity. The results of the theoretical investigations are in qualitative agreement with the experimental results.

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