doi:10.2533/chimia.2008.652 CHIMIA **2008**, *62*, No. 7/8

Organic Chemistry **377**

Pd/NHC-Catalyzed Asymmetric Intramolecular α-Arylation Reactions

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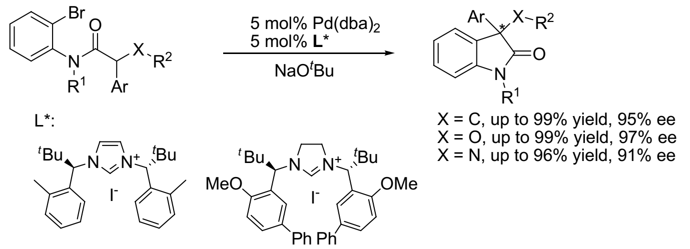
The palladium-catalyzed intramolecular α-arylation reaction of amides provides an efficient synthetic access to oxindoles. For the asymmetric version, many chiral ligands have been screened in the reaction and, prior to our study, the highest enantioselectivity reached was 76%. [1]
We have developed new chiral *N*-heterocyclic carbene ligands (NHCs) for this reaction. Their application in Pd-catalyzed reactions allows asymmetric oxindoles to be accessed efficiently and with high asymmetric induction. This includes, for the first time, also products with heteroatoms at the stereogenic center.[2,3]



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Physical Chemistry **379**

Competition between Charge Injection and Reductive Quenching at the Surface of Dye-Sensitized Semiconductors

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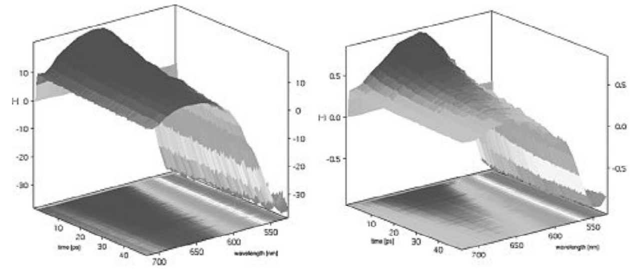
Aiming at the development of dye sensitized solar cells, photoinduced electron transfer at the surface of dye-sensitized semiconductors has been widely studied. Kinetic heterogeneities of the charge injection have been revealed and related, among other, to dye aggregation [1].



Comparison of the dynamics of Ru(II) complex dye excited states on alumina films (into which the dye doesn't inject) in the presence of reducing species (right) and in pure solvent (left), confirms that reductive quenching of the excited dye state by iodide does constitute an independent electron transfer pathway.
The time scale for such a process is in the order of tens of picoseconds and can indeed efficiently compete kinetically with other reactions involving the dye excited state, like the electron injection in titanium dioxyde.

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Organic Chemistry **378**

A Novel Strategy towards the Total Synthesis of Rhazinilam Analogue

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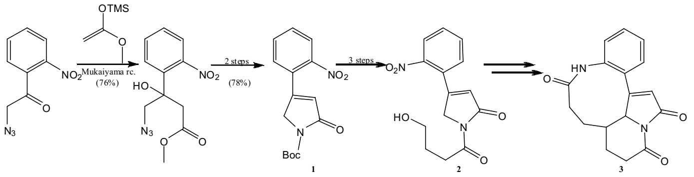
The alkaloid rhazinilam shows significant *in vitro* cytotoxicity, but no activity was found *in vivo* [1]. Our synthetic strategy is to replace, in the first time, the pyrrole ring by a corresponding pyrrole-2(5*H*)-one ring [2] using Mukaiyama crossed aldol reaction followed by Staudinger reaction. *N*-acylation and deprotection of **1** give the alcohol **2**. The planned synthesis of rhazinilam analogues of type **3** should be available using the strategy developed by the group of Banwell [3].



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Physical Chemistry **380**

From Radical Chemistry to Autoxidation Catalysis

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The liquid-phase oxidation of hydrocarbons such as cyclohexane and *p*-xylene are important processes in the chemical industry.[1] Despite their importance, the fundamental chemistry was not yet fully understood. Under the reaction conditions, the slow direct reaction of O_2 with the hydrocarbon is outrun by a much more efficient radical chain mechanism. It is generally accepted that the hydroperoxide is formed in a fast propagation reaction of chain carrying peroxyl radicals with the hydrocarbon substrate, whereas the alcohol and ketone were assumed to be formed in the slow termination reaction between two peroxyl radicals. This established vision is however at odds with several experimental observations. Based on a jointly combined theoretical and experimental study,[2-5] the hitherto overlooked, but very fast propagation of the hydroperoxide was recently identified as the predominant source of the ketone and alcohol product. The product distribution of various hydrocarbons can be readily rationalized by the rate of ROOH propagation, and the efficiency of the subsequent activated cage reaction.[3] During the presentation, several examples of catalyst design, based on this revised mechanism, will be discussed.

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Physical Chemistry **381**

Time/space-resolved IR and Raman investigation of dynamic surface-bulk events under operando NOx storage-reduction conditions

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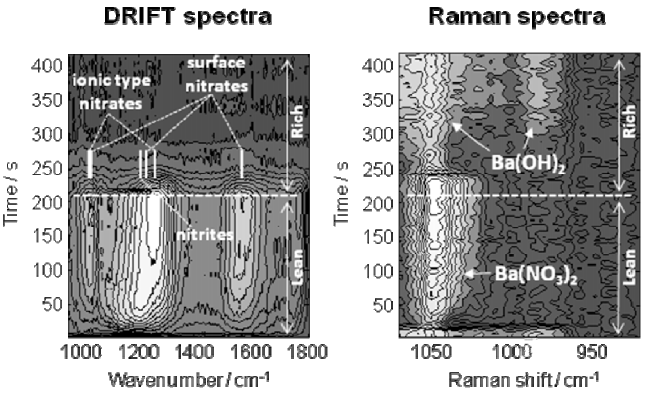
In situ analyses of dynamic surface and bulk events in heterogeneous catalysis are of immense importance to provide insights into mechanistic aspects of catalytic reactions. Time/space-resolved DRIFT and Raman spectroscopies were applied to study both surface and bulk species of Pt-Ba/CeO_2 catalyst under operando NO_x storage-reduction conditions, i.e., repeated lean ($NO/O_2/He$) – rich (H_2/He) gas cycles. A clear correlation of DRIFT spectra with Raman spectra was demonstrated with excellent time and space resolution. The combined surface sensitive (DRIFTS) and bulk sensitive (Raman) approach facilitates the firm understanding of complex dynamic surface and bulk processes, widely observed in heterogeneous catalysis.



Physical Chemistry **382**

Strong Level Mixing in Pulse EPR and Application to a Model System for Myoglobin (Mb) and Hemoglobin (Hb)

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Pulse EPR techniques provide information about the local environment of an unpaired electron and are increasingly used to elucidate the function of metal ions in biological systems. Recent advances in this field revealed that the consideration of strong level mixing is substantial in structure determination [1-4]. Unwanted effects, which are often negligible, - such as cross-suppression [2,3] and implicit-TRIPLE [4] - can sometimes dominate and strongly distort pulse EPR spectra of an electron coupled to many nuclei. In extreme cases this leads to complete cancellation of certain signals. As a consequence, biologically important nuclei or interactions can remain undetected for decades or may be misassigned in distorted spectra. Our recent study of Co-Mb and a synthetic model system showed that dioxygen adducts of cobalt containing porphyrins with one axial nitrogen base exhibit severe level mixing at standard experimental conditions (X-band frequencies) preventing the detection of distal hydrogen bonding [1]. Based on thorough analysis of the origins of strong level mixing these problems can now be circumvented by advanced pulse EPR techniques, optimized experimental conditions, and by an appropriate choice of the excitation frequency [1-3].

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Physical Chemistry **383**

Dissociative electron attachment in alcohols and ethers: The relationship between Rydberg states and Feshbach resonances

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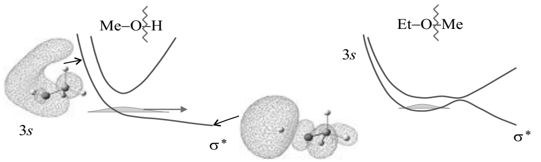

Most of the dissociative electron attachment (DEA) processes in saturated compounds are mediated by Feshbach resonances with temporary occupation of Rydberg-like orbitals, but little is known about their detailed mechanism. We gained insight into these processes in a comparative study of saturated compounds with the alcohol and the ether groups [1-3].

The results of this study reveal a dramatic difference in the dissociation patterns of Feshbach resonances in alcohols and in ethers. Whereas the O–H bond cleavage in alcohols proceeds already from the lowest Feshbach resonance, the C–O bond cleavage in ethers proceeds only from the higher-lying Feshbach resonances. From this observation we conclude that the lowest Feshbach resonance, $^2(n,3s^2)$, is dissociative in the alcohols but bound in the ethers.

The calculated potential curves for the Rydberg states along the dissociation coordinate were found to explain the observed spectral properties. The potential curves of Feshbach resonances will be calculated using the R-matrix theory.

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Physical Chemistry **384**

Generating highly active sites during oxidation of carbon monoxide

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The oxidation of carbon monoxide is one of the most intensely studied reactions in heterogeneous catalysis. The preferential oxidation of carbon monoxide in a hydrogen-rich mixture is an important reaction in fuel cells [1]. Determination of the structure of the catalytically active sites in oxidation of carbon monoxide, nitric oxide, and other hydrocarbons is relevant to automotive catalysts [2]. Work on single crystals of platinum showed that there are two reaction regimes, which have different rates. These differences arise from different surface reconstructions [3]. We have determined the catalytically active species during the oxidation of carbon monoxide over a real alumina-supported platinum catalyst under atmospheric pressure by combining in situ high-energy resolution fluorescence detection x-ray absorption spectroscopy [4] and kinetic measurements. The oxidation of carbon monoxide occurred in two distinctive regimes, a high-activity regime and a low-activity regime, which have high and low rates of reaction respectively. Oxidized platinum constitutes the active phase of the catalyst in the high-activity regime. In the low-activity region, the catalyst is poisoned by carbon monoxide, limiting the dissociative adsorption of oxygen. We bridged the material and pressure gaps and showed that different phases are active under high pressure in nano-sized catalyst particles.

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Physical Chemistry **385**

Performance of hierarchical mesoporous mordenite in the alkylation of benzene with benzyl alcohol

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The performance of zeolites can be improved by the introduction of mesopores into the zeolite micropore network. We prepared a hierarchical mesoporous mordenite by acid and alkali leaching [1] of a conventional mordenite synthesized by ourself, and characterized it by XRD, N_2 physisorption, SEM, and 2-methyl-2-pentene isomerization. The XRD and N_2 physisorption data showed that the leaching of mordenite gives a mesoporous material with MOR framework. The S_{BET} increased from 384 to 524 m^2 g^{-1} and the V_{meso} from 0.003 to 0.166 ml g^{-1}. The SEM images showed good crystallinity and the 2-methyl-2-pentene isomerization indicated that the mesoporous mordenite possessed stronger acidity than the conventional mordenite.

The benzylation reaction of benzene by benzyl alcohol was used to evaluate the catalytic reactivity of the hierarchical mesoporous mordenite in Friedel-Crafts alkylations [2]. The hierarchical mesoporous mordenite had a much higher catalytic activity than the conventional mordenite. At 80 °C and under atmospheric pressure, the conversion of benzyl alcohol by hierarchical mesoporous mordenite was close to 100% after 3 hours, whereas the conversion by conventional mordenite was only 1%. These results indicate that hierarchical mesoporous mordenite has potential application in Friedel-Crafts alkylations, especially of large molecules.

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Physical Chemistry **386**

Molecular catalysis for oxygen reduction at liquid liquid interface

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Developing nonnoble catalysts toward oxygen reduction to replace expensive platinum-based catalysts is one of the major approaches being explored to reduce the cost.[1] Metalloporphyrin complexes of cobalt, iron and manganese have been synthesized and their electrocatalytic behavior for a rapid two- or four-electron reduction of dioxygen has been studied.[2] In the present work, we show that the oxygen reduction by decamethylferrocene (DMFc) at a polarized water|1,2-dichloroethane (1,2-DCE) interface could be catalyzed by free base porphyrins, octaethylporphyrin (H_2OEP) and 5,10,15,20-tetraphenylporphyrin (H_2TPP). H_2OEP and H_2TPP can facilitate the successive transfer of proton from water to 1,2-DCE, and the protonated forms catalyze the oxygen reduction by DMFc. The reaction has been studied by cyclic voltammetry, differential capacitance and surface tension measurements. Two-phase shake flask experiment controlled by various common ions has also been performed. The 1,2-DCE and aqueous phases after the reaction were characterized by the UV-visible spectroscopic measurement and colorometric titration with sodium iodide respectively, which shows that DMFc is oxidized to $DMFc^+$ and hydrogen peroxide is found in the adjacent aqueous phase.

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Physical Chemistry **387**

Atomistic Simulations of CO and Methane Clathrate Hydrates

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Clathrate hydrates are formed by water arranged in an ice-like structure around guest molecules. A large variety of clathrates with different guest molecules have already been observed. The crystalline structure of clathrates suggests physical properties similar to those of ice. In contrast, it was found that the thermal conductivity is rather comparable to amorphous material.[1] The thermal energy in solids is transported via the lattice vibrations, characterized in clathrates by strong couplings between the guest and the host lattice.[2]

To study the influence of different guest molecules on the host lattice, methane and CO are chosen as a test case. Experimentally, formation of the same clathrate structure type has been observed for these two guest molecules. Molecular dynamics (MD) simulations are used to investigate the properties of methane and CO hydrates. The force field used for the simulations includes anharmonic bond potentials and accurate molecular electrostatics based on distributed multipoles[3,4]. Structural properties and lattice motions of the two systems are analyzed and compared.

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Physical Chemistry **388**

State-Resolved Reactivity of CH_4 on Pt(111) and Ni(111): Transition State Location and Structure

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Transition metal based catalysts are used in steam-reforming which converts CH_4 and H_2O into H_2 and CO. The key step in this process is the dissociative chemisorption of CH_4 on the catalyst surface. In order to obtain more detailed information about the dissociation of methane, we performed state-resolved reactivity measurements of CH_4 on Ni and Pt single crystal surfaces. We obtain information about the difference in transition state (TS) location for CH_4 dissociation on Pt(111) and Ni(111) by comparing the reactivity of the vibrational ground state and $2\nu_3$ excited state of methane on these two metals [1]. Since we find vibrational energy to be more efficient in promoting the reaction on Ni(111) than on Pt(111), we propose that dissociation on Ni(111) occurs via a "later" barrier than on Pt(111). This corresponds to a TS structure for which the dissociating C-H bond of CH_4 is stretched more strongly on Ni(111) than on Pt(111), in agreement with theoretical work [2]. We also investigated if the chemisorption of CH_4 on the Pt(111) surface depends on the particular vibrational motion of CH_4. Comparison of state-resolved reactivities of CH_4 in the $2\nu_3$ and $\nu_1+\nu_4$ states, shows that combining stretching and bending excitation in CH_4 is more efficient than exciting CH_4 with a ~40% more energetic pure stretching motion. This result is consistent with TS structure calculations of CH_4 on a Pt cluster performed by Psofogiannakis *et al.*[3].

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Physical Chemistry **389**

Infrared Laser Assisted Photofragment Spectroscopy on Biomolecules

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The combination of mass spectrometry and laser spectroscopy is used to investigate properties of biological ions in the gas phase. Closed-shell biomolecular ions are produced by a nanoelectrospray source, mass-selected by a quadrupole and guided into a 22-pole ion trap where they are cooled by collisions with helium buffer gas to less than 10 K. While stored inside the trap, the ions interact with laser light. Our detection scheme is based on photofragment spectroscopy: the molecules must dissociate for us to be able to detect the absorption of a photon. If the dissociation process is statistical, the fragmentation time scale increases with the molecular size.

Infrared laser-assisted photofragment spectroscopy (IRLAPS) was originally developed to measure high vibrational overtone spectra of molecules cooled in a supersonic free-jet [1, 2]. We use this technique here to increase the dissociation rate of biomolecules subsequent to electronic excitation by a UV laser. A fraction of the excited molecules undergoes internal conversion, reaching highly-excited vibrational states of the electronic ground state. A CO_2 laser pulse pumps the vibrationally excited ions to an energy above the dissociation threshold, causing them to fragment into daughter ions.

We present here the electronic and vibrational spectrum of two peptides, Ac-Phe-$(Ala)_5$-Lys and Ac-Phe-$(Ala)_7$-Lys-$(Pro)_2$-$(Ala)_5$-Lys, obtained using the IRLAPS technique.

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Physical Chemistry **390**

Steps toward experimental detection of molecular parity violation in CHFBrI: High resolution rovibrational analysis of the ν_6 mode

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The experimental detection of molecular parity violation [1] is of great interest for fundamental aspects of molecular dynamics and symmetries. Recent theoretical progress has led to the striking increase for predicted values of the parity violating energy difference between enantiomers of chiral molecules, $\Delta_{PV}E$, by one to two orders of magnitude [2]. An experiment for measuring $\Delta_{PV}E$ has been proposed some time ago [3], but an alternative consists also in measuring rovibrational frequency shifts in the infrared spectra of enantiomers [1,4,5]. A value of 50 mHz is predicted for vibrational frequency shifts in CHFBrI [5]. The FTIR spectrum of CHFBrI was recorded at 190 K and 295 K in the region 600-1300 cm^{-1} with an instrumental resolution of better than 0.001 cm^{-1} [6]. We were able to analyse the rovibrational spectra of $CHF^{79}BrI$ (ν_0 = 1060.81569 cm^{-1}) and $CHF^{81}BrI$ (ν_0 = 1060.77864 cm^{-1}) in the CF-stretching region. We will discuss line coincidences with CO_2 laser lines. In addition, we will show how submm wave spectroscopy based on the FAst Scan Submillimeter Spectroscopic Technique (FASSST) and phase-locked backward wave oscillators can be used to determine line shifts in the mHz region [7].

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Physical Chemistry **391**

Spin-orbit interaction and Jahn-Teller effect in the $X^+\ ^2E$ ground state of CH_3Cl^+

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The X ^2E ground state of CH_3Cl^+ is subject to the combined effects of a Jahn-Teller distortion along the e vibrational modes (ν_4, ν_5, ν_6) and a spin-orbit interaction [1]. He I photoelectron spectra of CH_3Cl have provided information on the vibrational structure but the assignments remain tentative and contradictory.

So far no high-resolution spectra of CH_3Cl^+ have been reported. We present the PFI-ZEKE photoelectron spectrum of the rovibrational structure of the $CH_3Cl^+\ X^+\ ^2E \leftarrow CH_3Cl\ X\ ^1A_1$ transition and its analysis using a rovibronic model that simultaneously treats the spin-orbit coupling and the linear Jahn-Teller effect and is based on Refs. [2,3].

The molecular constants derived in the analysis of the spectrum provide a description of the structure and dynamics of CH_3Cl^+ in its electronic ground state.

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Physical Chemistry **392**

Photodissociation dynamics of the 2-methylallyl radical

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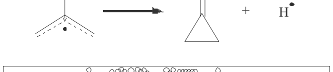
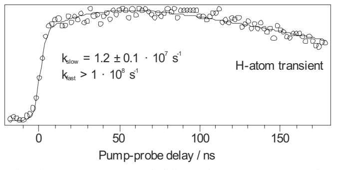
The dissociation dynamics of hydrogen atom loss from small hydrocarbon radicals following electronic excitation is currently not fully understood. It is generally assumed that the main dissociation pathway is unimolecular dissociation after ultrafast internal conversion. Recent experiments with ethyl[1] and allyl[2] have been performed in our group. In this study we focus on time- and frequency-resolved photoionization of the hydrogen atom product from a jet-cooled electronically excited 2-methylallyl radical, C_4H_7.





The measured dissociation rates and kinetic energy release of 2-methylallyl and its isotopologue $CD_3C_3H_4$ combined with high level *ab initio* calculations suggest unimolecular dissociation with methylenecyclopropane and hydrogen as the major C–H bond fission channel. Other possible dissociation and isomerization pathways are discussed[3] based on the results of the coupled-cluster *ab initio* calculations.

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Physical Chemistry **393**

Deperturbation of the $b\ ^3\Pi_g$ Electronic State ($v' = 0, 1, 2$) of C_2 by Two-Color Resonant Four-Wave Mixing

Peter Bornhauser, Peter P. Radi*

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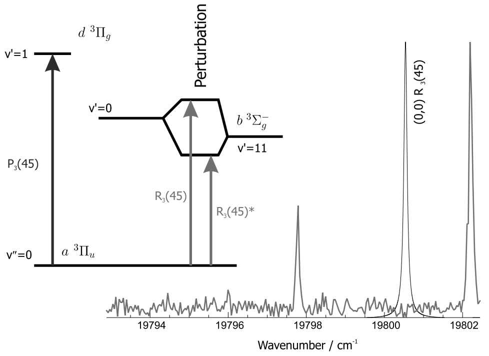
Analysis of perturbed rotational levels is often hindered due to numerous overlapping transitions present in absorption or emission spectra. By applying two-color resonant four-wave mixing [1], unambiguous assignment of the perturbed levels is possible via intermediate level labeling.



The measured data yield coupling constants and characterize the interaction mechanism. Simultaneously, deperturbed molecular constants are obtained for the interacting vibrational levels of the $b\ ^3\Sigma_g^-$, $B\ ^1\Delta_g$ and $B'\ ^1\Sigma_g^+$ electronic states of C_2.

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Physical Chemistry **395**

Time–resolved studies of Electronically Excited Radical Ions in Liquid Solution

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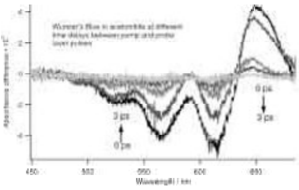
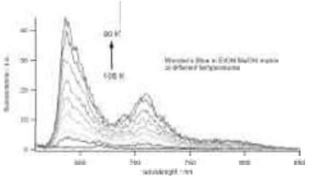
Little is known so far about the photophysics of radical ions, especially about the excited state dynamics since most of the studies published come from low–temperature matrix experiments and are not time resolved.

We investigate radical ions in liquid solution at room temperature by means of femtosecond transient absorption spectroscopy. For the generation of the radical ions we use two completely distinct approaches: On the one hand we use salts of persistent radicals like, e.g., Wurster's Blue, on the other hand we employ an on–line electrochemical flow–through cell for less persistent radicals.





Ultrafast relaxation within hundreds of femtoseconds to a few picoseconds was found for all the radical ions investigated so far. This is surprising since the energy difference between the ground state and the lowest excited state is substantial. A quite high density of electronic excited states is common for all of these ions and therefore a conical intersection with the ground state is probable. This hypothesis is also supported by the observation of an unusual temperature dependence of the fluorescence of Wurster's Blue.

Physical Chemistry **394**

Three-Point Frequency Fluctuation Correlation Functions of the OH-Stretch of Liquid Water

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Characterizing the dynamics of the OH stretch in isotopically substituted liquid water (HOD in D2O) in terms of 3-point frequency fluctuation correlation functions and joint probability densities shows that dynamics during hydrogen bond rearrangements occur primarily along a coordinate which is perpendicular to the spectroscopic coordinate. Molecular dynamics simulations show that 3-point correlation functions are sensitive to this motion, unlike 2-point correlation functions, and can select sets of trajectories which linger in the area of the transition state. [1] 3D-IR correlation spectroscopy could potentially measure these dynamics, though motional narrowing significantly changes the shape of the resulting spectra; we will report ongoing experimental progress.

[1] S. Garrett-Roe, P. Hamm *J. Chem. Phys.* **2008**, *128*, 104507.

Physical Chemistry **396**

High Resolution Infrared Spectroscopy of Small Heterocyclic Chiral Biomolecular Precursor Molecules

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Molecular parity violation has been critically discussed in relation to early biochemical evolution [1] and in this context precursor molecules of evolution might be of interest [2,3]. Here we report initial results from a high resolution spectroscopic study of the three-membered heterocyclic molecules aziridine-2-carbonitrile ($C_3H_4N_2$) and oxiranecarbonitrile (C_3H_3NO). The highly resolved infrared spectra of chiral molecules are complicated, difficult to record, and challenging to assign because of their complex structure, and most of the high resolution infrared studies have been performed in our group [4,5], including those of the three-membered heterocyclic ring compounds d_1-oxirane and fluoro-oxirane [7]. The work reported here expands upon this foundation. There is also interest in the astrophysical observation and isomerization reactions in these systems [3,6].

[1] M. Quack, *Angew. Chem. Intl. Ed. (Engl.)* **2002**, *41(24)* 4618.
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[5] S. Albert and M. Quack, *ChemPhysChem*, **2007**, *8,* 1271.
[6] G. S. Tschumper, *J. Chem. Phys.* **2001**, *114(1),* 225.
[7] K. K. Albert, S. Albert, M. Quack, J. Stohner, O. Trapp, V. Schurig, *Proc. 19th Coll. High Resol. Mol. Spectr., Salamanca* **2005**, 248. H. Hollenstein, D. Luckhaus, J. Pochert, M. Quack and G. Seyfang, *Angew. Chem.-Int. Edit. Engl.* **1997,** *36(1-2),* 140.

Physical Chemistry **397**

Electronic structure of Triazinetriphosphonic Acid Dimethoxy Esters: EPR and DFT studies

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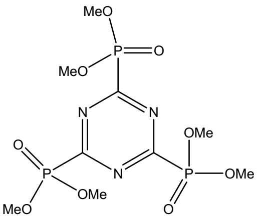
In the context of material sciences, Triazinetriphosphonic Acid Dimethoxy Esters (I) presents two interesting proprieties:

1) electron-acceptor behaviour due to the presence of the triazine ring.
2) transition-metal complexing agent due to the presence of the $(MeO)_2P=O$ groups.



(I)

The cyclic voltammogram of the compound is characterized by a reduction wave at -1.0 V vs. Ag/Ag+. Electrochemical reduction of Triazinetriphosphonic Acid Dimethoxy Ester leads to EPR spectra exhibiting hyperfine interaction with three ^{14}N and three ^{31}P nuclei. These isotropic coupling constants agree with those predicted by DFT calculation for the corresponding radical monoanion by assuming fast exchange between various conformations. As shown by the SOMO, the unpaired electron is delocalized on the whole Π system.

Physical Chemistry **398**

The high resolution infrared spectrum of phenol: First rovibrational analysis of the modes ν_4 and ν_{17b}

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One of the great challenges of high resolution infrared spectroscopy is to understand the rovibrational resolved spectra and the dynamics of large molecular systems involving numerous degrees of freedom and large amplitude motions such as bending, torsion or inversion modes [1]. Through the coupling of such modes complicated resonance networks can be built up and the energy flow can be studied upon excitation [2,3]. As a benchmark molecule we discuss phenol. Its infrared spectrum already vibrationally assigned at low resolution [4], was measured in the range 600-1300 cm^{-1} with our Bruker ZP2001 spectrometer [5] with a resolution of better than 0.001 cm^{-1}. We obtained a rotationally resolved eigenstate spectrum and present a rovibrational analysis of the out-of-plane modes ν_4 (ν_0 = 687.00544 cm^{-1}) and ν_{17b} (ν_0 = 881.70033 cm^{-1}). Here, no torsional splittings or resonances were observed. We will discuss the *J*-dependent doublets ranging from 0.01 to 0.014 cm^{-1} observed in the rovibrational spectra of the OH-bending mode (ν_0 = 1176.3 cm^{-1}) and an A_1 mode at ν_0 = 807 cm^{-1} tentatively assigned as $2\nu_{18b}$. We interpret these doublets as torsional splittings. A comparison of the phenol and fluorobenzene spectra will also be given.

[1] S. Albert and M. Quack, *ChemPhysChem*, **2007**, 8, 1271, M. Quack. *J. Mol. Struct.*, **1995**, 347, 245.
[2] H. R. Dübal and M. Quack. *J. Chem. Phys.*, **1984**, 81(9), 3779. M. Quack., *Ann. Rev. Phys. Chem.*, **1990**, 41, 839.
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Physical Chemistry **399**

Ultrafast Second Harmonic Generation from Triphenylmethane Dyes at the air/water Interface

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The interface is that special region which provides the bridge between two different bulk media. The asymmetry of forces is at the origin of its unique chemical and physical properties. Consequently, it is not surprising that the interfacial processes can strongly differ from those in the bulk.
In this work, the excited-state dynamics of malachite green oxalate (MG) at the air/water interface measured by the surface specific time-resolved second harmonic generation has been compared to the bulk dynamics determined by transient absorption. Comparison between the two sets of results allows surface exclusive phenomena to be recognized.

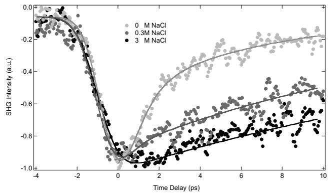

Figure 1: Time resolved SHG of malachite green oxalate at the air/water interface with various NaCl concentrations.

Figure 1 shows the time profiles of the SHG intensity recorded with different concentrations of NaCl in water. The observed dynamics reflects the recovery of the ground-state population of MG upon a non-radiative transition process involving large amplitude motion of the phenyl rings. While bulk measurements point to a very small salt effect on the ground state recovery dynamics, substantial differences can be observed at the air/water interface. We interpret these changes in terms of salting-out effect induced by sodium chloride. This effect leads to an enhancement of the interfacial MG concentration, which favours aggregation of the dyes and a slowing down of the ground-state recovery dynamics. The influence of other ions with differents salting-out properties has also been investigated. Prelimary results indicate a trend opposite to that expected according to the Hofmeister series [1].

[1] W. Kunz, P. Nostro, B.W. Ninham, Current Opinion in Colloid and Interface Science 9 (2004) 1.

Physical Chemistry **400**

Sub Doppler resolution laser spectroscopy of C_2H_2 using double resonance methods

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The investigation of parity violation in chiral molecules is of great interest in physics and chemistry [1,2]. Several high-resolution experiments were proposed and performed to measure the very small parity violating frequency shift between IR bands of two enantiomers of CHFClBr [3]. However, this shift is calculated to be extremely small [4]. Another promising experiment is to observe the time evolution of an initially prepared state with well-defined parity [5,6]. In this time resolved method the excited state with well-defined parity has to be populated in a multi-step preparation process [5,6]. In preparation for this experiment, a stabilized OPO-laser system was set up for optical/optical double resonance experiments. Double resonance techniques allow for Doppler free spectroscopy and states are accessible, to which direct transitions from the vibrational ground state are forbidden, through the population of an intermediate level. We report the high-resolution rovibronic analysis of the vibrational level $\nu_1+2\nu_3$ of C_2H_2 using the ν_3 vibrational state as an intermediate level. This provides a proof of principle of the first steps in the pumping scheme.

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Physical Chemistry **401**

A Terahertz Time-Domain Spectroscopy Study of the Complex Conductivity of Hole Conducting Materials

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Replacing the conventional solvent-based electrolyte in dye sensitized solar cells [1],[2] by redox active ionic liquids [3], hole conducting molecular liquids or amorphous solid hole conducting materials could lead to an increase in long term stability. In this work, dc-conductivity measurements, viscosity measurements and terahertz time-domain spectroscopy are used to characterize the conductivity in a frequency range from about 100 GHz to 2.6 THz under various temperature conditions

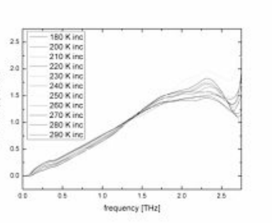

Figure 1: Real conductivity computed from THz-TDS of PMII/I_2 ionic melt with an iodine concentration of 3.28M. Data were taken by increasing the temperature.

Especially the dependence on iodine concentration of the conductivity in a PMII/I_2 melt was investigated, because a surprisingly high dc-conductivity despite a high viscosity of the medium, was observed, suggesting conductivity mechanisms other than simple ionic diffusion.

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Physical Chemistry **403**

Photophysical Properties of Ruthenium(II) Complexes with TTF-PPB Bridging Ligand

Nathalie Dupont,[a] Claudia Leiggener,[a] Christine Goze,[b] Elvira Beitler,[b]
Shi-Xia Liu,[b]
Silvio Decurtins,[b] and Andreas Hauser[a]

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We studied the photophysical properties of the $[\{Ru(bpy)_2\}_n(TTF\text{-}ppb)](PF_6)_{2n}$ (n=1,2)complexes(TTF-ppb 4',5'-bis-(propylthio)tetrathiafulvenyl[*i*]dipyrido[2,3-*a*:3',2'-*c*]phenazine, (see Fig. 1). At room temperature in solution, the complexes show three intense absorption bands in the visible (see Fig. 2), which can be readily attributed to specific charge transfer (CT) transitions. The absorption bands at 23800 and 15100 cm^{-1}correspond to the metal to ligand CT transition Ru(II) → bpy and Ru(II) → ppb, respectively. The band at 12500 cm^{-1} is assigned to the intraligand CT (ILCT) on TTF-ppb (TTF → ppb). Compared to the spectrum of the free ligand, the ILCT band is red-shifted to a larger extent going from mononuclear to dinuclear complexes, due to a lowering of the energy of the LUMO by reducing the electron density on the aromatic ppb ring system [1]. The free ligand shows luminescence from the ILCT state which is quenched in the mono- and dinuclear complexes. In order to have a better knowledge of the quenching mechanisms, their photophysical measurements upon chemical or electrochemical oxidation, are under investigation.

[1] C. Goze, E. Beitler, N. Dupont, C. Leiggener, H. Jia, P. Monbaron, S.-X. Liu, A. Neels, A. Hauser, S. Decurtins, *Inorg. Chem.* 2008, submitted.

Physical Chemistry **402**

Real-time investigation of peptide dynamics

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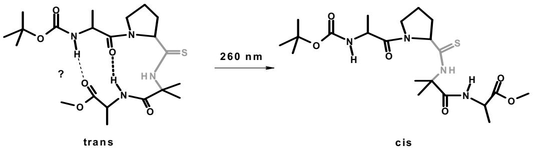
To investigate dynamics of a peptide during a conformational change, photo switches integrated into the backbone of the peptide can be used as a trigger. Here we use the substitution of an oxygen atom in one peptide bond by a sulphur atom, which red-shifts the $\pi\rightarrow\pi^*$ excitation with respect to the non-substituted peptide bonds. This unit can then be excited selectively at 260 nm. Significant photoisomerization of the thiopeptide bond for N-Methylthioacetamide (the simplest isomerizing molecule with a substituted peptide bond) and in thiopeptides up to 20 amino acids has been reported[1][2]. The β-turn forming thiopeptide Boc-Ala-Pro(thio)-Aib-Ala-OMe was characterized by time-resolved infrared spectroscopy, steady-state FTIR-spectroscopy and ^{1}H-NMR.



The thiopeptide shows an open and a hydrogen bonded conformation in its thermal equilibrium. The opening of the bonded species upon isomerization of the photo switch is completed after one nanosecond. This structural change has been inverstigated by transient two-dimensional infrared spectroscopy.

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Physical Chemistry **404**

Methane Combustion over Pd-doped $LaFeO_3$

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La-Fe-Pd perovskites used for automotive applications were shown to prevent sintering of the precious metal under operating conditions through a continuous incorporation/segregation process [1]. Aiming at using such materials for CNG engine applications, we prepared perovskites of the formula $LaFe_{1-x}Pd_xO_3$ (x = 0.05, ca. 2 wt.% Pd) by the citrate method by adding the Pd salt to the precursors solution ($LaFe_{0.954}Pd_{0.046}O_3$) and by impregnation of $LaFeO_3$ (Pd/$LaFeO_3$). All calcined samples (SSA: 14 m^2/g) exhibited only $LaFeO_3$-reflections. XRF measurements exhibited a Pd-L_α-fluorescence line in the $LaFeO_3$-matrix with lower intensity than on the surface. EXAFS spectra of calcined samples indicated the presence of only Pd-O bonds with no Pd-Pd contribution from PdO nanoparticles. An additional hint to the incorporation of Pd is provided by the activity data toward methane combustion (1 vol.% CH_4-20 vol.% O_2-He). The highest catalytic activity was found for the impregnated sample (2 wt.% Pd/$LaFeO_3$, $T_{50\%}$: 430°C; $LaFeO_3$, 507°C; $LaFe_{0.954}Pd_{0.046}O_3$, 518°C). Pd/$LaFeO_3$ reduced at 200°C exhibited lower activity (445°C) compared to the unreduced sample but was still more active than $LaFe_{0.954}Pd_{0.046}O_3$. The data indicate that Pd significantly improved the activity of $LaFeO_3$, but the Pd incorporated into the perovskite lattice did not promote CH_4-combustion.

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Physical Chemistry **405**

Absolute cross sections for the dissociative electron attachment to HCl, HBr and their deuterated analogs

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We present dissociative electron attachment cross-section measurements for HX and DX (X= Cl and Br). We have utilized a trochoidal electron monochromator with a recently constructed total ion collection collision chamber. The chamber can be used in two independent modes of measurement - in the “no ion extraction” mode, the created ions hit the collection sheets due to their large gyroradii; in the “active ion extraction” mode a small electrostatic voltage is applied across the chamber and ions are collected due to the electric field.

Electron attachment to both hydrogen halides leads to the production of X^- at low electron energies, below 1 eV, and to the production of $H^-(D^-)$ at higher energies, around 7 eV. The experimental cross section for the X^- production was compared with the predictions of the nonlocal resonance theory [1]. Whereas the theoretical results agree with our measurements in case of Br^-/HBr, the model seems to overestimate the cross section for Cl^-/HCl by approximately a factor of 3. Both HBr and HCl cross sections show a strong isotope effect, however, this effect is much weaker for the $H^-(D^-)$ production than for the X^- production.

[1] J. Horáček, M. Čížek, P. Kolorenč and W. Domcke, *Eur. Phys. J. D* **35**, 2005**,** 225

Physical Chemistry **406**

EPR and DFT studies of TTF-triazine compounds

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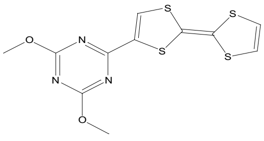
30 Quai Ernest Ansermet, 1211, Geneva, Switzerland



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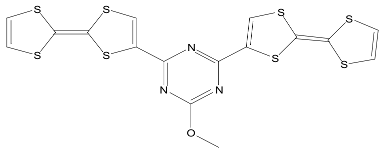

2

Cyclic voltammetry shows that the first oxidation of dimethoxy-tetrathiafulvalene-triazine (1) occurs at 0,65V. Both electrochemical and chemical oxydation of 1 lead to an EPR spectrum characterized by a clearly resolved hyperfine structure with the protons of the TTF moiety (two equivalent protons A_{iso} = 2,24 MHz, one additionnal proton A_{iso} = 3,16MHz). The electronic structure of the resulting radical cation is discussed in the light of DFT calculations, at the performed B3LYP-IGLOIII level. These results are used to interpret the voltammograms and EPR spectra obtained by oxidation of 2.

Physical Chemistry **407**

Gold-catalyzed aerobic oxidation of alcohols: Effect of gold particle size on catalytic performance in different solvents

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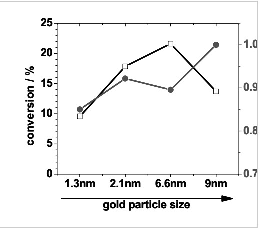
Department of Chemistry and Applied Biosciences, ETH Zürich, Hönggerberg, HCI, CH 8093 Zürich, Switzerland)

Colloidal gold – larger colloids are often referred to as Purple of Cassius – is known and used for centuries and various recipes have been described, e.g. in Libavius’ chemistry book “Alchemia” published in 1597. In the present contribution, the effect of the size of gold particles deposited on CeO_2 and TiO_2 supports on their catalytic behavior in the aerobic oxidation of alcohols in different solvents has been investigated. For the preparation of the catalysts, gold colloids were synthesized by the reduction of $HAuCl_4$ by tetrakis(hydroxymethyl)phosphonium chloride (THPC). The Au particle size was controlled in the range 1.3 – 11.3 nm. The size of the colloids was determined by means of EXAFS measurements and by taking HAADF-STEM images from the colloids in solution as well as from the Au/support systems to validate the conservation of the Au particle size. An optimum particle size for the oxidation of benzyl alcohol is found at higher particle diameter ($d \approx 6.9$ nm) compared to CO oxidation [1] which is catalyzed by smaller Au nanoparticles. Identical trends for the activity – particle size relationship were found when the reaction was monitored at atmospheric pressure using mesitylene as a solvent as well as under supercritical conditions for CeO_2 and TiO_2.



[1] Haruta, *Catal. Tod.* **1997**, 36, 153

Physical Chemistry **408**

Picosecond Time-Resolved Vibrational Circular Dichroism Spectrometry

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Vibrational circular dichroism (VCD) is the difference of absorption of a vibrational transition between left and right circular polarized infrared light. Being intrinsically sensitive to the molecular structure via the coupling of vibrational modes, VCD can yield precious information on the conformation of biomolecules and has been, for example, successfully used to distinguish helical from unfolded domains in polypeptides [1]. Extension of this technique to the recording of time-resolved VCD spectra is therefore very promising as it may enable us to observe chiral intermediates in fast chemical reactions or to follow the dynamics of conformation changes in peptides and proteins in unprecedented detail. Here we report on the first pulsed laser set-up which is capable of recording both static VCD spectra and photo-induced changes in VCD signals with picosecond time resolution [2]. An amplified femtosecond laser system is synchronized to a photoelastic modulator to produce alternating left- and right-handed circular polarized mid-IR pulses at 1 kHz repetition rate. Transient changes in vibrational circular dichroism of the CH-stretch vibrations of the cobalt-sparteine complex $Co(sp)Cl_2$ were recorded in a first proof-of-principle experiment.

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[2] Mathias Bonmarin, Jan Helbing, “A picosecond Time Resolved Vibrational Spectrometer” Submitted (2008)

Physical Chemistry **409**

Nanoporous photocathode and photoanode for light energy conversion

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In recent years, the fabrication of novel ultrathin film systems featuring multi-functionalities has been extensively studied because of their potential applications in electronics, photonics, sensors and photoelectrochemical cells. The goal of the present work was to develop film-modified electrodes for light energy conversion applications. Three-dimensional thin photoactive films were fabricated by a layer-by-layer assembly of positively charged polyelectrolytes (poly-L-Lysine, pLys) and negatively charged semiconductor nanoparticles (NPs) on a carboxylic acid terminated alkanethiol-modified gold electrode. Two types of NPs were used to build uniform films: Cadmium Selenide (CdSe) and Cadmium Selenide/Cadmium Sulfide core/shell (CdSe@CdS). The film growth was monitored by UV-vis absorption and fluorescence measurements. The charge carrier dynamics was monitored by fluorescence lifetime measurements using time correlated single photon counting (TCSPC). The photoelectrochemical properties of the films immersed in an organic electrolyte solution are determined by photocurrent measurements. Large photocathodic and photoanodic currents were recorded for CdSe and CdSe@CdS sensitized films, respectively. The photocurrent magnitude increases with the number of NPs layers. A theoretical model of the photocurrent responses was developed to analyse the kinetics of photo-induced processes and coupled reactions.

[1] Authors Names, *Journal Abbr.* **2000**, *30*, 1111.
[2] (Times 12 pt normal)

Physical Chemistry **410**

Combined high resolution FTIR and jet-diode laser spectroscopic study of $PFCl_2$: Rovibrational analysis of the PF-stretching mode ν_1

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In order to increase the pool of chiral molecules for the study of molecular parity violation [1], we have extended our investigation towards isotopically chiral molecules [2]. We have started by analyzing the high resolution infrared spectra of isotopically chiral molecules like $CH^{35}Cl^{37}ClF$ [3-5], d1-oxirane [6] and $PF^{35}Cl^{37}Cl$ [2]. Here we present first results of $PFCl_2$. Its spectra have been measured with our diode laser spectrometer in a jet at 15 to 20 K in the regions 830-834 cm^{-1} and 838-841 cm^{-1} and with our Bruker ZP 2001 prototype spectrometer [5] with a resolution of 0.001 cm^{-1} in the range 650-1000 cm^{-1} at room temperature. We were able to analyse the hybrid *c/b*-type band structure of the PF-stretching mode of $PF^{35}Cl_2$ at ν_0=836.61484 cm^{-1}. However, this band is strongly perturbed in both isotopomers by a Coriolis-type resonance through the ν_3+ ν_5 band. The cold diode laser spectra at 15 K simplified the spectra considerably. Therefore we were able to detect absorption lines of the ν_1 band of the isotopic chiral molecule $PF^{35}Cl^{37}Cl$ in the cold spectra. We present an assignment of this band. In addition, we will discuss our jet-diode laser spectrometer in detail and show the improvements made in the meantime to earlier versions [3] of this setup.

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Physical Chemistry **411**

Structure sensitivity of the Rh-catalyzed enantioselective hydrogenation of activated ketones

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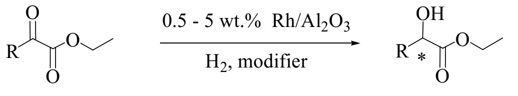
Hydrogenation of unsaturated compounds on (supported) metal catalysts is commonly considered as a structure insensitive reaction [1]. Former studies on metal-catalyzed enantioselective hydrogenations provided contradictory results [2]. Here we prepared a series of Rh-on-alumina catalysts with 0.5-5 wt.% metal loading by flame synthesis. The catalysts were characterized by STEM and by a DRIFT study of CO adsorption, and tested in the enantioselective hydrogenation of α-ketoesters in the presence of cinchona alkaloids. With increasing metal loading the Rh particle size increased from 1 to 2 nm and the fraction of oxidized to metallic Rh at the surface of the particles decreased. Parallel to this shift, also the initial reaction rate and enantioselectivity increased by a factor of up to ten, depending on the substrate, the modifier, and the reaction conditions. The unprecedented structure sensitivity may originate from the strong metal-support interaction that varies with the metal particle size and probably affects the adsorption of the substrate-modifier complex on the metal surface.



R = Me or *i*-Pr

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Physical Chemistry **412**

Calculation of Scalar Couplings across Hydrogen Bonds by MMPT potential

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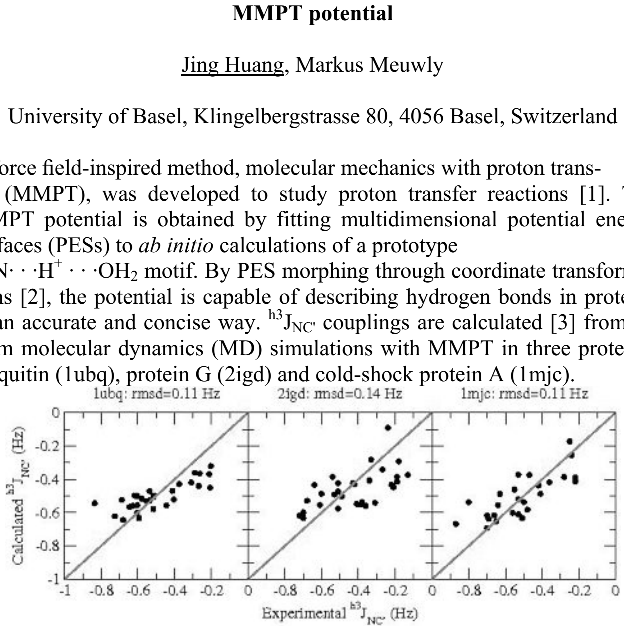
A force field-inspired method, molecular mechanics with proton transfer (MMPT), was developed to study proton transfer reactions [1]. The MMPT potential is obtained by fitting multidimensional potential energy surfaces (PESs) to *ab initio* calculations of a prototype $H_3N\cdot\cdot\cdot H^+\cdot\cdot\cdot OH_2$ motif. By PES morphing through coordinate transformations [2], the potential is capable of describing hydrogen bonds in proteins in an accurate and concise way. $^{h3}J_{NC'}$ couplings are calculated [3] from all atom molecular dynamics (MD) simulations with MMPT in three proteins: ubiquitin (1ubq), protein G (2igd) and cold-shock protein A (1mjc).



Compared to previous results using conventional force fields using constraints such as SHAKE or RATTLE (RMSD~0.15Hz), better agreement between calculated and experimentally determined $^{h3}J_{NC'}$ scalar couplings has been achieved. In addition, we will concentrate on different ways of PES morphing and treating different hydrogen bonds (αhelices, β sheets, loops) separately.

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Physical Chemistry **413**

Electron driven chemistry in saturated oxygen containing compounds

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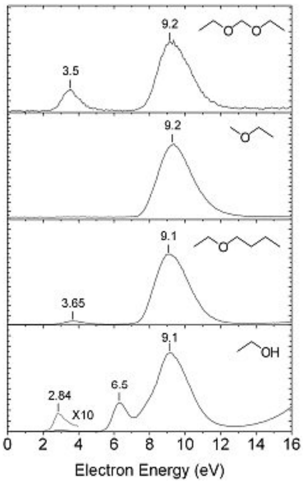
Dissociative electron attachment (DEA) is an important process in electron –molecule collisions. Interest in DEA is due to new emerging applications in technology, for example the Focused Electron Beam Induced Processing (FEBIP) [1], and the need to understand radiation-induced damage to living tissue [2].



To gain insight into the dissociation mechanism we have performed a comparative study of several alcohols and ethers [3,4]. Our current study reveals an interesting case of site selective chemistry in compounds with ether bonds. The fragmentation occurs at an energy independent of the target molecule but depends on which neutral alkyl fragment is lost. The dissociation energies are: 8.0 eV for loss of butyl, 8.5 eV - propyl and 9.1 eV - ethyl.

We conclude that the excitation in the Feshbach resonances (a hole and two electrons in a Rydberg-like orbital) is largely localized on the respective alkyl groups.

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Physical Chemistry **414**

Investigation of the Mn(Salen)Br-catalyzed synthesis of cyclic organic carbonates by *in situ* X-ray absorption spectroscopy at the Mn-K and Br-K edge

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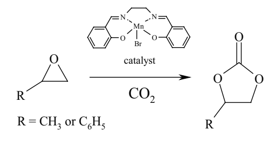
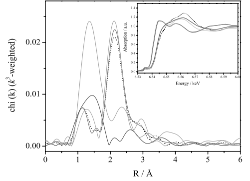
The solvent-free synthesis of useful cyclic organic carbonates from epoxides and CO_2 has gained considerable interest triggered by environmental concerns. Among others, N,N'-bis(salicylidene)ethylenediamino (salen) complexes of Mn(III) have shown to be effective catalysts for this reaction, especially when also bearing a bromo ligand [1].

The mechanism of this reaction and similar catalytic systems however still remains speculative. Since the reaction only takes place under elevated pressure and temperature conditions (45-55 bar, 353-413 K), *in situ* spectroscopic investigation of such high pressure systems is required.





In the present study, we employed a specially designed spectroscopic high pressure batch cell to investigate this reaction *in situ* at the Synchrotron beamline. Complementary measurements at both the Mn-K and the Br-K edge allowed simultaneous analysis of the two key components of the catalyst, the Mn(III) metal centre of the complex, and the Br^- ligand. The results of this investigation shed some light on the reaction mechanism [2].

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Physical Chemistry **415**

Excited-state dynamics of naphthalene diimide based multichromophoric systems

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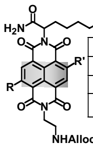
Swizerland

Multichromophoric compounds consisting of amino naphthalene diimides (NDI) covalently attached to a p-octiphenyl scaffold have been shown to self-assemble as supramolecular tetramers in lipid bilayer membranes and to enable generation of a transmembrane proton gradient upon photoexcitation. Moreover the photo- and electrochemical properties of the NDI systems can be tuned by varying the substituent on the NDI core (see Figure 1).



R	R′	Colour
NHPr	NHPr	blue
NHPr	Cl	red
OEt	OEt	yellow

Figure 1. Structure of NDI core with different substituents.

Using femtosecond time-resolved spectroscopy we evidence the formation of a charge-separated state upon excitation of octachromophoric NDI systems with three different substituents. Two charge separation (CS) pathways have been evidenced: symmetry-breaking CS between two NDI units and CS between NDI and the scaffold. We found that the lifetime of the charge separated state that is responsible for their photoactive properties depends on several parameters such as the number of chromophoric units and the NDI substituents. The origin of these effects will be discussed in detail.

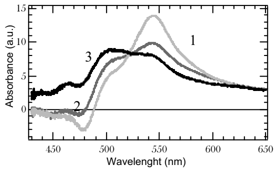


Figure 2. Intensity-normalized transient absorption spectra of yellow monomer (1), dimmer (2) and octamer (3). The spectrum of (1) is due to the locally excited state, while that of (3) is due to the charge-separated state.

Physical Chemistry **416**

Potential energy functions of the six lowest electronic states of $ArKr^+$

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The pulsed-field-ionization zero-kinetic-energy (PFI-ZEKE) photoelectron spectrum of the ArKr mixed rare-gas dimer has been recorded between 108000 and 120000 cm^{-1} (1 eV = 8065.544 cm^{-1}). This spectroscopic technique in combination with a narrow-bandwidth laser source allows the determination of the energy levels of an ion with respect to these of its parent neutral molecule with an accuracy of better than 1 cm^{-1}.

The ground state of the dimer is almost repulsive ($D_e \approx 116$ cm^{-1} [1]), but in several excited and ionic states the dimer is strongly bound [2, 3, 4]. The Rydberg and ionic states have been accessed by 1+1′ resonance two-photon excitation via an intermediate state located below the $Ar(^1S_0)$ + $Kr(5p[1/2]_0)$ dissociation limit.

Lines corresponding to transitions to many vibrational levels of the X(1/2), $A_1(3/2)$ and $A_2(1/2)$ states were observed in the wavenumber region 108000-113000 cm^{-1}. Using the positions of vibrational levels of the X(1/2), $A_1(3/2)$ and $A_2(1/2)$ states and transition energies reported in [5, 6, 3] the positions of the vibrational levels of the B(1/2), $C_1(3/2)$ and $C_2(1/2)$ could be predicted.

A semiempirical potential model describing these six ionic states which includes the effects of the spin-orbit, charge-exchange and long-range interactions was used to define potential energy functions for the six low-lying electronic states of $ArKr^+$ that reproduce all experimental observations.

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Physical Chemistry **417**

In Situ Spectroscopic Study of the Hydrothermal Ageing of Rh-based Model Three-Way Catalysts

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Hydrothermal ageing is a facet of the general ageing phenomenon observed in the exhaust exiting the car engine. As prepared and hydrothermally aged 2 wt.% Rh/Al_2O_3 have been chosen as models to study the ageing of the Rh-component of TWC. The catalysts have been characterized using BET, XRD, TEM and XPS. Whereas ex situ characterization of materials is only partially able to give information on structural changes induced by ageing, in situ DRIFT and XAS studies revealed the most promising to characterize the structural and reactivity differences of the metal under working conditions. Both techniques indicated that hydrothermal ageing (700°C, 16 h, 20% humidity) causes Rh to be in a state which is more resistant to reduction. The as prepared material showed extensive reduction already at room temperature and after treatment at 400°C in hydrogen, whereas the aged sample still exhibited oxidised Rh domains. The reduction of NO by CO was chosen as test reaction [1-4] both for in situ DRIFT and XAS. Ageing affected mostly the selectivity, the aged catalyst exhibiting higher selectivity to N_2O at ca. 250°C that can be related to the different oxidation state of Rh.

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Physical Chemistry **418**

Accurate rotational constants of three benzene isotopomers by femtosecond rotational coherence spectroscopy

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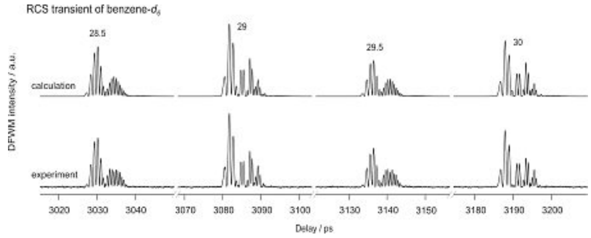
Benzene is one of the prototype molecules in chemistry and the knowledge of its structural parameters to very high accuracy is of particular interest. Gas phase molecular structure information can be obtained from the analysis of the rotational constants, however, for the non-polar isotopomers of benzene these are not accessible via microwave spectroscopy. Femtosecond time-resolved rotational coherence spectroscopy yields very high accurate rotational constants of molecules exhibiting no permanent dipole moment [1]. This technique has been applied to benzene-d_6 by Jarzeba *et al.* [2]; we present revised measurements for benzene-d_6 with higher accuracy, and compare to the infrared spectroscopic value of Snels *et al.* [3]. In addition we measured the rotational and centrifugal distortion constants of benzene-h_6 and 1,3,5-trideuterobenzene to very high accuracy.



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Physical Chemistry **419**

Direct Femtosecond Observation of Tight and Loose Ion Pairs upon Photoinduced Bimolecular Electron Transfer

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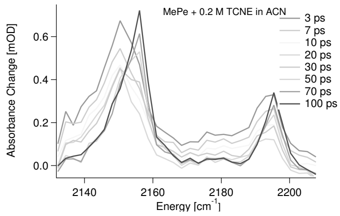
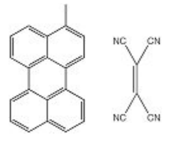
A driving force dependent reaction distance is usually invoked to explain the absence of the Marcus inverted regime in photoinduced bimolecular charge separation (CS), leading to solvent separated or loose ion pairs (LIP) at high exergonicity, in contrast to contact or tight ion pairs (TIP) at low exergonicity.





Using femtosecond near IR spectroscopy we can for the first time distinguish such different types of ion pairs by their distinct spectral signatures. The figure depicts the transient absorption of the asymmetric CN stretch vibration of the tetracyanoethylene anion generated upon ET quenching of 3-methylperylene as a function of time delay after excitation. Our results show that the controlling parameter for obtaining tight vs. loose ion pairs is rather the ground state equilibrium between isolated reactants and complexed donor-acceptor pairs than the driving force for CS. Anisotropy observed on the bands attributed to TIPs indicates that ultrafast CS into TIPs if favoured by a coplanar geometry of the donor-acceptor pairs, thus demanding refinement of theoretical models which rely on spherical reaction species that solely involve reaction distances.

Physical Chemistry **420**

Systems Including the Containers and Resolution of Gibbs Paradox

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When mixing and demixing are considered in studies of hydrophobic effect and porous structure, "containers" must be considered as part of the system under study. For solid mixtures, component A can be taken as the containers component B. However, thermodynamics normally treats the fluid (gases, liquids or solutions) body as the concerned system. The heat engine system considered in thermodynamics does not include the container. What is worse, Gibbs Paradox [1] states that the separation of the porous medium to form a bulky fluid phase and a pure bulky solid phase would not lead to any change in thermodynamic parameters; these two structures are of the same stability, which, intuitively, must be wrong. Applying information theory concepts, recently carried out active studies lead to the resolution of Gibbs paradox [2-4].

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DOI: 10.3390/entropy-e10010001. arXiv:0803.2571.

Physical Chemistry **421**

Generation of tunable Fourier-transform-limited terahertz pulses using narrowband near-infrared laser radiation

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Fourier-transform-limited pulses of terahertz (THz) radiation (bandwidth of $\sim$10 MHz, peak power up to $\sim$300 μW) have been generated using a crystal of the highly nonlinear organic salt 4-N,N-dimethylamino-4′-N′-methyl stilbazolium tosylate (DAST) [1] in a collinear, normal-incident configuration. Outputs from two narrowband ($\Delta\nu < 1$ MHz, $\lambda \sim$800 nm) cw titanium-doped sapphire (Ti:Sa) ring lasers with a well-controlled frequency difference were shaped into pulses using acousto-optic modulators (AOM), coupled into an optical fiber, pulse amplified in Nd:YAG-pumped Ti:Sa crystals and used as optical sources to pump the DAST crystal, which was cut along the *b* axis to fulfill the phase-matching condition. THz output power can be further enhanced by optimizing the angle of incidence in most of the frequency region. Pulsed radiation up to 11 THz has been detected with a 4.2 K germanium bolometer. The absorption spectra of H_2O from 0 to 11 THz and a pure rotational transition of hydrogen fluoride (HF) near 5 THz were recorded. The experimental results using the cut DAST crystal will be compared with those using other THz emitters including (i) as-grown (*c*-cut) DAST crystals, (ii) zinc telluride (ZnTe) crystals, (iii) gallium phosphide (GaP) crystals, and (iv) low-temperature-grown gallium arsenide (LTG-GaAs) photomixers with THz spiral antennas.

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Physical Chemistry **422**

Accurate structure of cyclooctatetraene by femtosecond rotational coherence spectroscopy and ab initio calculations

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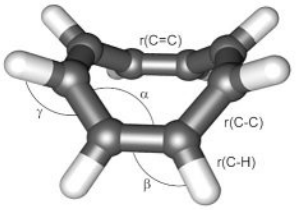
Femtosecond time-resolved rotational coherence spectroscopy and high-level *ab initio* calculations are used to obtain accurate structural information for the nonplanar antiaromatic molecule 1,3,5,7-cyclooctatetraene (C_8H_8, COT) and its perdeuterated isotopomer COT-d_8 (C_8D_8). We measured the rotational B_0 and centrifugal distortion constants D_J, D_{JK} of the v=0 states of both isotopomers, e.g., B_0(COT)=2710.329(56) MHz, B_0(COT-d_8)= 2283.318(88) MHz and B_v for the v=1 states ν_6, ν_{11}, ν_{17}, ν_{22} and ν_{41}/ν_{42} of COT [1]. The experimental rotational constants are compared to those obtained from calculations at the CCSD(T) level. Combining the experimental and calculated rotational constants with the calculated equilibrium bond lengths and angles allows to determine accurate equilibrium structure parameters, i.e., r_e(C-C)=147.02(5) pm, r_e(C=C)=133.7(1) pm, r_e(C-H)=107.9(1) pm, α_e(C-C-C)=126.55(1)°, β_e(H-C=C)=117.70(1)° and γ_e(H-C-C)=115.61(1)° [1].



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Physical Chemistry **423**

Accuracy in high resolution and high sensitivity spectroscopy: predissociation lifetime in $(HF)_2$ by means of CRD spectroscopy

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Molecular beam techniques combined with continuous-wave cavity ring-down spectroscopy (cw-CRDS) provide a powerful tool to measure very weak absorptions of isolated molecules with very high resolution and sensitivity. This method has been successfully developed in our group and used to measure combination bands of nitrous oxide, chloroform, and methane [1-3], as well as $(HF)_2$ [4]. We have been able to measure and analyze the *N*=2 triad of this important dimer involving excitations with two quanta of HF stretching [4] and to estimate the predissociation lifetime of $(HF)_2$ τ_{PD} for these excitations. Under our jet expansion conditions, a Voigt profile, i. e., a convolution between a Gaussian (from a reduced Doppler effect) and a Lorentzian (from the predissociation lifetime of the dimer) profile, is well suited to reproduce the profile of the rotational lines [4]. The determination of the two components has revealed to be a delicate matter. Indeed some measurements have led to different τ_{PD} for transitions involving the same excited state [4].

Since these measurements, the experimental setup has been fully overhauled and allows for measuring weaker absorption with a better signal to noise ratio at colder beam temperatures [5]. We propose here to systematically re-measure some lines and perform a full width analysis to investigate the influence of the fit procedure on the τ_{PD} value and get better estimation of the origins of the error in the measurement.

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Physical Chemistry **424**

Hydrogen Bonding Interactions in Cinchonidine - 2-Methyl-2-Hexenoic Acid Complexes

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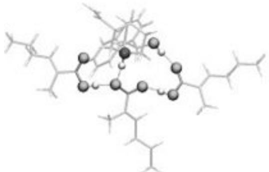
The molecular interactions between cinchonidine (CD) and 2-methyl-2-hexenoic acid (MHA) were investigated using a combined spectroscopic and theoretical approach. These interactions are of particular interest due to their pivotal role in the chiral induction occurring in the heterogeneous catalytic asymmetric hydrogenation of α,β-unsaturated acids. NMR experiments revealed the structural confinement of CD upon MHA addition via specific hydrogen bonding interactions. The characteristic symmetric and asymmetric carboxylate stretching vibrations of the CD-MHA complex were studied by ATR-IR modulation excitation spectroscopy (MES). The spectra were compared with the simulated spectra of energetically stable CD-MHA complexes, suggested by DFT calculations. Spectroscopic and theoretical results indicated a dynamic equilibrium between hydrogen bonded CD-MHA complexes with a CD:MHA ratio of 1:2 and 1:3, with a strong preference for the 1:3 complex formation [1]. (Figure: 1:3 halfN cyclic, the most stable CD-MHA complex) The entropic stabilization by the specific hydrogen bond network was clearly reproduced by *ab initio* molecular dynamics.



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Physical Chemistry **425**

Reversible Phase Transition in Buckybowl Monolayers: Direct Observation of Supercooling Effects.

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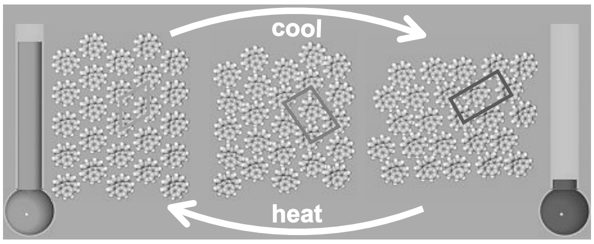
Many chemical compounds exist in more than one crystalline form. The control of polymorphism is of vital importance in food processing, pharmaceutics, speciality chemicals and even data storage. Although solid-solid phase transitions have been observed for almost 200 years, they are still poorly understood. Phase changes in 2 dimensions should be easier to understand and can be directly observed at a molecular level with scanning probe microscopy.

We present a study of corannulene ($C_{20}H_{10}$), a curved fullerene fragment molecule with C_{5v} symmetry, adsorbed on a Cu(111) surface. At room temperature corannulene forms a regular 4×4 overlayer on the substrate. Upon cooling the molecular layer transforms into a much denser crystal phase. With further cooling, a third stable crystal layer is observed (see figure). The transition is fully reversible: by increasing the temperature, the 4×4 structure is formed again. This phase transition is directly observed with scanning tunnelling microscopy. The observation of the effects of supercooling the high-temperature phase at a molecular level allows new insights into the mechanisms of solid-state phase transitions.



Physical Chemistry **426**

Isotope selective overtone spectroscopy (ISOS) of $^{12}C_6HD_5$, $^{13}C^{12}C_5HD_5$ and $C_6H_5NH_2$ measured in a molecular beam

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The analysis of high resolution overtone spectra can provide insight into the intramolecular vibrational energy redistribution (IVR) in benzene and its deuterated species and other substituted derivatives [1-4]. The analysis of the IR-spectra and the determination of vibrational couplings can be considered as complementary to a time resolved observation of the IVR processes [5]. We report the spectrum and the vibrational analysis of the fundamental and first overtone of the CH-stretching vibration of rotationally cooled pentadeuterated benzene $^{12}C_6HD_5$ and several isotope-isomers of $^{13}C^{12}C_5HD_5$ measured by ISOS. In addition we report the absorption spectra of the N=3 polyad of the NH-chromophore. As in the measurements of the N=2 polyad [4] for the vibrational temperature obtained in the molecular beam only the absorption lines for the transition from the lower level of the inversion doublet could be found if seeding with Ar was used. The spectra are compared to recent results from room temperature spectra and theoretical calculations [6-8].

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Physical Chemistry **427**

Pocket transfer study of NO ligand in truncated hemoglobin

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Since their discovery in prokaryotes and unicellular eukaryotes, the truncated hemoglobins (trHbs) have received significant experimental as well as computational attention [1]. One of the well studied hosts of the trHbs, the *Mycobacterium tuberculosis*, is the causative agent of human tuberculosis [2]. The crystal structure of the trHbN of *M. tuberculosis* has been shown to have a continuous tunnel through the protein matrix ideally suited for diatomic ligand movement [3]. Little is known about ligand migration pathways in heterogeneous environments such as a protein since it is a transient phenomenon and is difficult to follow with direct experimental methods. In the present study, atomistic simulations have been performed to study nitric oxide (NO) migration in the trHbN of *M. tuberculosis*. From extensive molecular dynamics simulations, the structural and energetic properties of the ligand docking sites in the protein have been characterized and a connectivity network between the ligand docking sites has been built. The energetic estimations for ligand migration among these pockets are provided. For an accurate electrostatic description of the NO ligand in the protein environment, the recently developed three-point fluctuating charge model for dissociated NO has been employed [4], which correctly describes the variation of the dipole and quadrupole moments of the ligand as the bond length fluctuates. Also are calculated the infrared spectra of NO molecule situated in different ligand docking sites of the protein which allows spectroscopic characterization of the protein pockets, assignment of structural features associated with protein-ligand interactions, and predictions for experimental verification.

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Physical Chemistry **428**

Experimental and Theoretical Investigation of the Polarization Dependence of NO Rydberg Spectra

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The results of an investigation of high-n Rydberg spectra of nitric oxide by resonance-enhanced multiphoton excitation using circularly polarized radiation are presented.

Starting from the X $^2\Pi_{1/2}$ ($v''' = 0,\ J'''$) vibronic ground state and using a three-photon three-color excitation scheme via the A $^2\Sigma^+$ ($v'' = 1,\ J''$) and the H $^2\Sigma^+$, H' $^2\Pi$ ($v' = 0,\ J'$) intermediate states, nf Rydberg series converging to different rotational levels of the X$^+$ $^1\Sigma^+$ ($v^+ = 0,\ J^+$) vibronic ground state of the cation were recorded in the range of principal quantum number $n = 30 - 80$. np Rydberg series have not been observed, presumably because of the strongly predissociative nature of NO np Rydberg states. The lifetimes of the nf states were measured as a function of the strength of an applied electric field. The transition intensities to the Rydberg states as well as to the H,H' intermediate states show a strong dependence on the polarization of the incident light.

The ability to record and interpret spectra using different incident light polarizations promises to be a valuable tool in the assignment of more complex spectra [1]. Also, circularly polarized light is thought of as being a key component of the extension of an existing Rydberg Stark deceleration scheme [2] to nonhydrogenic atoms as well as to molecules.

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Physical Chemistry **429**

The state of Ru in Ru-hydroxyapatite during aerobic oxidation of benzyl alcohol

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Hydroxyapatite is a stable and recyclable support of heterogeneous catalysts employed in organic synthesis. The partial replacement of Ca^{2+} ions in the lattice of hydroxyapatite with 1–4 valent metal ions affords different classes of materials. Ru-substituted hydroxyapatites have shown remarkable activity in the liquid phase aerobic oxidation of alcohols [1]. The structure of Ru has been investigated using ATR-IR spectroscopy under close to reaction conditions. The infrared data obtained upon oxidation-reduction cycles and ^{12}CO and ^{13}CO adsorption in the presence of cyclohexane support the existence of a hydrated RuO_x-like phase, identified by overtone signals of Ru-O bonds at ca. 1850 cm^{-1} and likely organized as a two-dimensional phase on the apatite. This phase coexists with isolated Ru^{3+} cations likely located in the hardly accessible channels of the apatite structure. The RuO_x-like phase is shown to be highly reactive at the solid-liquid interface and exhibits a number of carbonyl species upon CO adsorption. The relevance of this phase for the oxidation of benzyl alcohol has been investigated. The detection of benzaldehyde signals, although weak, makes the results relevant to draw structure-activity relationships. Blocking of accessible Ru sites using CO prior to reaction reveals that only selected CO species on the hydrated RuO_x-like phase are depleted when reaction occurs. Furthermore, the enhanced formation of HCO_3^- in the absence of the alcohol indicates that benzyl alcohol oxidation and HCO_3^- formation may occur on similar Ru sites, providing evidence that these sites are located on the RuO_x phase.

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Physical Chemistry **430**

The Pentad and the Octad of $^{13}CH_4$: Lines in the 2200-4700 cm^{-1} Region

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We have carried out new high resolution measurements of infrared spectra of the spherical top molecules $^{12}CH_4$, $^{13}CH_4$ and $^{12}CD_4$. The spectra have been taken in the range 1800-8000 cm^{-1} at low temperature (80K) and at room temperature (298K) using the Zürich prototype Bruker 125 spectrometer (ZP 2001) in combination with a low temperature cooling cell [1]. Low temperature, giving rise to a reduced Doppler full width at half maximum (factor of 1.91) and very high resolution (0.0027 cm^{-1} for spectra in the region around 3000 cm^{-1}), made it possible to determine line positions very accurately, i.e. better than $10^{-4}cm^{-1}$ around 3000 cm^{-1}. We have studied $^{13}CH_4$ spectra in its pentad region [2] (2250-3250 cm^{-1}). Now we are climbing up the polyad ladder into the octad region (3800-4750 cm^{-1}), recently analyzed for the isotopomer $^{12}CH_4$ [3]. We will present an initial analysis of this region counting 8 levels, discuss the observed strong interactions and compare to the work on $^{12}CH_4$ [3]. The complex interacting system is analyzed using an effective Hamiltonian theory described in [4].

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Physical Chemistry **431**

Absolute dissociative electron attachment cross sections for acetylene and diacetylene

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Although more than one hundred neutral molecules and cations have been recorded in the interstellar space so far, the first anions were reported only recently. The first identified anion was C_6H^- [1], followed by C_4H^- [2] and C_8H^- [3]. For addressing the question how the $C_{2n}H^-$ ions are formed, both in laboratory discharges and in space, the knowledge of the cross section for elementary processes in plasmas is necessary. We present the study of dissociative electron attachment to C_2H_2 and C_4H_2.

We utilized two complementary instruments: (i) a dissociative electron attachment (DEA) spectrometer providing a mass analysis of the created DEA fragments as a function of the incident electron energy and (ii) a newly constructed total ion collection tube providing absolute total DEA cross sections. At low electron energies that are present in the laboratory discharges, both molecules show DEA bands corresponding to the production of the $(M\text{-}1)^-$ molecular anions. In case of acelytlene the C_2H^- fragment peaks at 2.95 eV with a cross section of 3.6 pm^2, in fair agreement with the value of 2.2 0.3 pm^2 obtained by Azria and Fiquet-Fayard [4]. In diacetylene C_4H^- peaks at 2.5 eV with a cross section of 3.0 pm^2. At higher electron energies, additional bands are present [5], in this region diacetylene has a considerably higher DEA cross section.

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Physical Chemistry **432**

Supersonic jet spectroscopy of the 2-aminopyridine dimer

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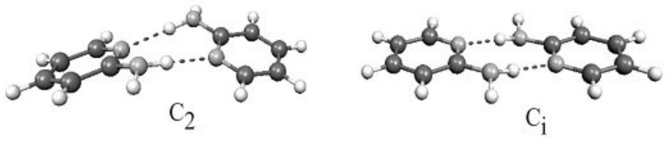
2-aminopyridine (2AP) is a structural mimic for the Watson-Crick hydrogen binding site of adenine and has been employed to investigate the physical properties of the hydrogen bonded DNA base pair analogues in the gas phase [1]. The excited state of the $(2AP)_2$ dimer exhibits a fast deactivation mechanism that has been interpreted in terms of a double proton transfer reaction [2].

Optimization of the $(2AP)_2$ structure using RI-MP2/aVTZ *ab initio* calculations reveals a fourfold minimum potential with two symmetry-equivalent C_i and C_2 minima each, and low interconversion barriers.

We have measured the infrared spectrum of jet-cooled $(2AP)_2$ in the 2600 - 3600 cm^{-1}, which fully supports the doubly hydrogen bonded structure. The band assignments of a previous IR study on $(2AP)_2$ [3] were extended and corrected.



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Physical Chemistry **433**

2-Pyridone·benzene: An N-H···π bonded T-shaped complex

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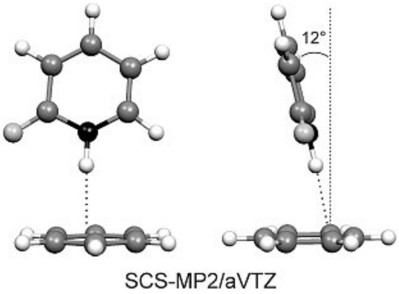
T-shaped and stacking interactions between π-conjugated molecules are of great importance in many biological systems (e.g., DNA, RNA, proteins). We have investigated the complex of the nucleobase analogue 2-pyridone (2PY) with benzene. Both MP2 and SCS-MP2 level ab initio calculations predict a slightly slanted T-shaped structure, bonded via a 2PY N-H···π interaction. Supersonic jet infrared spectra in the 1200 - 2000 cm^{-1} and 2800 - 3600 cm^{-1} ranges indicate that there is a significant interaction between the 2PY N-H group and the benzene moiety, while the interaction of the 2PY C=O group with benzene is very weak. This is in agreement with the computed T-shaped geometry. The experimental electronic origin of 2PY·benzene is red shifted compared to the origin of the 2-pyridone monomer. This feature also implies the absence of a hydrogen bond to the C=O group, since C=O hydrogen bonded 2PY complexes show blue shifted origins.



Physical Chemistry **434**

High-resolution electronic spectroscopy of the low-lying electronic states of XeKr and XeAr

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Informations on the low-lying electronic states of the heteronuclear rare-gas dimers XeRg (Rg=Kr, Ar) available in the literature are limited to the vibrational structure of several band systems in the VUV range of the electromagnetic spectrum (see for instance Refs [1, 2, 3]). Using a near-Fourier-transform-limited vacuum-ultraviolet laser system [4] spectra of the C $\leftarrow$ X and D $\leftarrow$ X band systems of several isotopomers of XeKr and XeAr were recorded at high resolution in the wavenumber range from $77\,000\,\text{cm}^{-1}$ to $77\,350\,\text{cm}^{-1}$ by resonance-enhanced two-photon ionization spectroscopy. The rotational and vibrational structures of C-X and D-X band systems could be fully resolved and assigned on the basis of isotopic shifts and combination differences. Potential energy functions and a full set of spectroscopic parameters were derived for the excited states. The poster will present the results of the analysis and compare them with the results of earlier investigations.

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

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Physical Chemistry **435**

Quantum dynamics on a model potential allowing for predissociation with and without coherent laser excitation

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Exponential decay is one of the primary chemical processes which is well known from classical kinetics. It has been derived by perturbation theory from first principles in the early days of quantum mechanics and could be derived also in an exactly solvable matrix coupling model by Bixon and Jortner [1]. One can find exponential decay of the initial wavepacket in the case of simple, exact harmonic oscillator dynamics [2], which illustrates the exponential decay of a Lorentzian distribution of equidistant states. There have been quantitative studies of femtosecond wavepacket motion of 'real' polyatomic molecules under coherent excitation [3].

In this work we report results on a predissociation potential with tunneling through a barrier. Populations of quantum states have been calculated and both the radiationless decay of a single initial resonance state as well as the decay induced by coherent infrared radiation has been studied within the weak field quasiresonant approximation (WFQRA) [4]. Exponential decay is observed at high enough densities of states outside the barrier region.

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Physical Chemistry **436**

Understanding Protein Adsorption Phenomena

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Protein adsorption on solid interfaces is an ubiquitous event when complex biological samples are analyzed. In biosensor applications it is typically considered as a serious problem as the non-specific adsorption on sensor surfaces degrades the detection sensitivity and selectivity. On the other side the efficiency of immuno-sensors may rely on an optimal orientation and organization of surface immobilized receptor proteins. In any case it is desirable to have a control over protein adsorption on surfaces which requires systematic investigations in this complex field.

Unlike small molecules the adsorption of proteins to interfaces is often accompanied by complex phenomena such as conformational re-orientations, transitions between different adsorbed states, overshootings, cooperative adsorption, or aggregation. Using Supercritical Angle Fluorescence (SAF) microscopy, a surface selective detection technique, we collected comprehensive experimental kinetic data that serve as a fundament of adsorption models. In particular, they provide precise mechanisms for the often observed effects of overshooting and cooperative protein adsorption which are subject of controversial debate. Further we characterized the in situ build-up of protein layers in the course of adsorption. Various surface features such as deposited protein clusters, regions of high and regions of low protein density were distinguished indicating that a perfectly homogeneous protein monolayer is usually an illusion. Applying the technique of intermolecular Fluorescence Resonance Energy Transfer (FRET) on protein clusters revealed a spreading mechanism that induces a flattening of the initially compact packing. In this way initially globular protein aggregates may become two-dimensional surface clusters after continued spreading. These insights into protein adsorption phenomena may help to find efficient strategies to control the behavior and organization of proteins covering interfaces.

Physical Chemistry **437**

Structure performance relations of supported metal catalysts

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To achieve a sustainable world economy, catalysts should be very active and selective. The catalysts of the future have a well defined structure to achieve the required performance. Nanoscience in catalysis has become a powerful technique to construct catalysts, which helps to understand structure-performance relations using in situ spectroscopy.

Heterogeneous metal catalysts are widely used in various reactions including selective hydrogenation, complete and partial oxidation, and reduction of NO_x with hydrocarbons. The catalytic performance of supported metal catalysts depends strongly on contact structure, support, particle size and metal alloying. All these factors can be separately studied by synthesis of catalysts with monodispersed metal particles supported on well defined supports and study them in different catalytic systems. To obtain monodispersed metal particles we synthesized Nanoparticle catalysts using controlled colloidal chemistry routes.

CO oxidation and epoxidation reactions are remarkably structure sensitive. The structures of the catalytically active sites and their interactions with the reactant intermediates will be determined using in situ spectroscopy under catalytically relevant conditions.

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Physical Chemistry **438**

Where atomic spectra are like molecular spectra: fine and hyperfine structure of high Rydberg states of xenon studied by millimetre wave spectroscopy and MQDT calculations

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In the range 0–45 cm^{-1} below the ionisation limit, the separation between adjacent electronic states (Rydberg states with principal quantum number $n > 50$) of atoms and molecules is smaller than 2 cm^{-1}. In order to resolve the fine and hyperfine structure of these states, very high resolution is needed. For most atoms and molecules, however, the direct access to Rydberg states from the ground state requires light in the UV or VUV range, and the spectral resolution is limited by the spectral bandwidth of the laser and/or the Doppler broadening. A significantly higher resolution can be obtained by combining a high-resolution laser system with millimetre radiation [1].

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

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

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Physical Chemistry **439**

Structure sensitivity in the enantioselective hydrogenation of ketopantolactone using Pt nanoparticles of well defined shape

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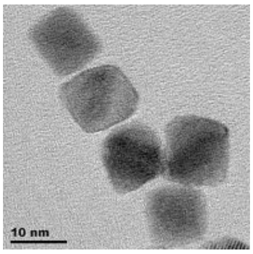
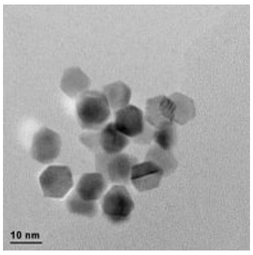
Silica supported Pt nanoparticles with controlled shape, as recently synthesized by El-Sayed et al. [1], were used to study the structure sensitivity of the hydrogenation of α-ketopantolactone in the presence of the cinchonidine [2]. The cubic particles of sample (a) with preferentially exposed (100) faces were more reactive, while sample (b) with a higher fraction of (111) faces gave slightly higher enantioselectivity (up to 75% ee). Prereduction of the catalyst improved activity and enantioselectivity on both samples indicating a restructuring of the Pt surfaces and/or the removal of surface impurities. Changes in the size and shape distribution of the metal particles were followed by electron microscopy (TEM/STEM), and IR spectroscopy was used to identify the relevant surface species.



(a)



(b)

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Physical Chemistry **440**

The $E\otimes(b_1\oplus b_2)$ Jahn-Teller effect in the allene cation studied by high-resolution photoelectron spectroscopy

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The first four torsional bands of the $C_3H_4^+$ $\widetilde{X}^+$ $^2E \leftarrow C_3H_4$ $\widetilde{X}$ $^1A_1$ transition of allene have been studies by pulsed-field ionisation (PFI) zero-kinetic energy (ZEKE) photoelectron spectroscopy. The electronically degenerate ground state of the cation is prone to a Jahn-Teller (JT) effect, which causes it to distort along the normal coordinates of b_1 and b_2 symmetry. This is a result of the $E\otimes(b_1\oplus b_2)$ JT effect characteristic of point groups with a four-fold symmetry axis. The JT distortion takes place along the modes ν_4 (torsion) and ν_6 (asymmetric C=C=C stretch). Until recently the spectroscopic information on the allene cation was limited to that contained in HeI photoelectron spectra [1,2]. We present here fully rotationally resolved PFI-ZEKE photoelectron spectra of allene. The rotational structure of the lowest two torsional bands is regular, ab the intensity distribution indicates a static distortion. The first adiabatic ionisation potential of allene was determined to be 78142.9 cm^{-1}.

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Physical Chemistry **441**

Generation of circularly polarized VUV laser radiation

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Multiphoton excitation with circularly polarized radiation is a convenient method to prepare nonpenetrating Rydberg states with $\ell \geq 3$ of an atom or a molecule. Long-lived hydrogenic Rydberg states can be generated in this way which can be studied by high resolution spectroscopy or used in Rydberg-Stark deceleration experiments [1-3].

Circularly polarized VUV laer radiation was generated by resonance-enhanced two-color sum-frequency mixing $\tilde{\nu}_{\mathrm{VUV}} = 2\tilde{\nu}_1 + \tilde{\nu}_2$ in a Xe jet using a linearly polarized UV laser beam ($\tilde{\nu}_1$) in resonance with the $\mathrm{Xe}\,5\mathrm{p}^5 6\mathrm{p}[1/2]_0 \leftarrow \mathrm{Xe}\,5\mathrm{p}^6$ two-photon transition and a circularly polarized visible laser beam ($\tilde{\nu}_2$). The purity of the polarization of the generated VUV laser radiation was determined making use of the selection rules for M_J ($\Delta M_J = \pm 2$ for circular light, depending on the polarization direction $\sigma_\pm$) in ${}^1\Pi_\mathrm{g} \leftarrow {}^1\,\Sigma_\mathrm{u}^+ \leftarrow {}^1\,\Sigma_\mathrm{g}^+$ two-photon transition in para H_2.

We performed the experiment on H_2 using a $1 + 1' + 1'$ doubly resonant three-photon two-colour REMPI procedure via the intermediate $\mathrm{B}\,{}^1\Sigma_\mathrm{u}^+(v' = 3, J' = 1)$ and $\mathrm{I}\,{}^1\Pi_\mathrm{g}(v = 0, J)$ states using two circularly polarized photons. The two-photon transition to the $\mathrm{I}\,(v = 0, J = 1)$ from the $\mathrm{X}\,(v'' = 0, J'' = 0)$ state via the $\mathrm{B}\,(v' = 3, J' = 1)$ state is allowed for all combinations of polarizations of the two laser beams except the one in which both laser beams are circularly polarized with the same helicity. This two-photon transition is therefore well suited to determine the purity of the VUV laser polarization which we show to be $> 85\,\%$.

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Physical Chemistry **442**

Intramolecular Redistribution of Vibrational Energy in Propargylhalides Measured by Femtosecond Pump-Probe Experiments

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The fast intramolecular redistribution of vibrational energy (IVR) is an important requirement to apply statistical methods in unimolecular reaction theory [1,2]. The time evolution of the vibrational wavefunction can be obtained from high-resolution IR-spectra or the IVR process can be studied directly in femtosecond pump-probe experiments [2-4]. We have set up a pump-probe scheme where the IVR dynamics is followed either by sensitive UV- or IR-absorption of the time delayed probe pulse. To increase the sensitivity of our experiments in the gas phase the two laser beams are confined in a hollow waveguide. From the overtone spectra it is well established that for propargyl halides the IVR process after excitation of the overtone of the CH-stretching vibration is different, depending on whether the methylenic $\mathrm{CH_2X}$-group or the acetylenic CCH-group is excited [3,5]. In accordance with the prediction from IR-spectroscopy the femtosecond pump-probe experiments show that the measured IVR times for the acetylenic CH-stretching vibration are larger by a factor 20-40 than the shortest time process detected after the excitation of the methylenic CH-stretching vibration.

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Physical Chemistry **443**

EPR and DFT studies of the radical cation $[\mathrm{Mo(CO)_5PPh_3}]^{\bullet +}$

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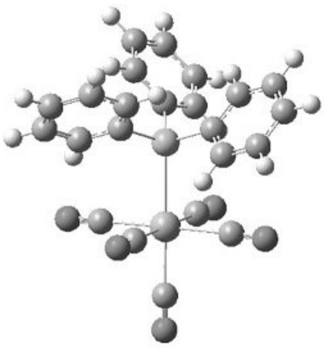

The radical cation $[\mathrm{Mo(CO)_5PPh_3}]^{\bullet\,+}$ has been trapped at 77 K in an irradiated single crystal of the neutral precursor. The resulting spectra are characterized by a large anisotropy of the g-tensor. Hyperfine interacting coupling with ${}^{95/97}\mathrm{Mo}$ and ${}^{31}\mathrm{P}$ nuclei are clearly observed and analysed in terms of spin delocalisation.

Quantum chemical calculations at DFT/B3LYP-IGLO-III level were performed to interpret the EPR results. ORCA package was used to estimate spin orbit coupling effects (SOMF) and relativistic contributions (ZORA).

Physical Chemistry **444**

Simple Analytical Simulations of PSA System for Binary Mixture c-$\mathrm{C_6H_{12}}$-$\mathrm{C_6H_5Cl}$ Adsorbed on Activated Carbon U-03 and Based on Adsorbed Amount and Kinetic Desorption Rate.

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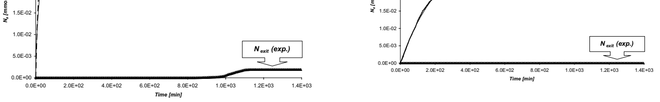
This study presents a simple simulation of pressure swing adsorption - PSA system for the adsorbed mixture of fully miscible components c-$\mathrm{C_6H_{12}}$-$\mathrm{C_6H_5Cl}$ adsorbed on activated carbon U-03. Simple simulations of PSA system is based on the adsorbed quantity N_o and the constants of desorption rate k obtained from single component desorption curves in dynamic experiments. The simulation verified by experimental results appeared also to be in good accordance with the analogical model reported by *Rebstein* [1].



Comparison of experimental curves (—) N_d*(exp.)* with simulation curves (- - -) N_d*(sim.)* obtained for c-$\mathrm{C_6H_{12}}$ (Figure A) and $\mathrm{C_6H_5Cl}$ (Figure B). Experimental outlet concentration curve N_{exit}*(exp.)* for both substances reflecting also breakthrough curve for c-$\mathrm{C_6H_{12}}$ (Figure A) is also included

Acknowledgements: Special thanks to Prof. Fritz Stoeckli (University of Neuchatel, Switzerland) for experimental and financial support granted by SNSF.

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Physical Chemistry **445**

Hydrogen Peroxide Generation by Decamethylferrocen at a Liquid|Liquid Interface

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An electrochemical method for producing hydrogen peroxide (H_2O_2) in the absence of any noble metal catalysts at a soft molecular interface rather than at a solid electrode is presented [1]. This approach relies on controlling the interfacial Galvani potential difference between two immiscible electrolytes, in other words the polarization at a lqiud|liquid interface, to allow the reduction of oxygen to H_2O_2. In this system, decamethyferrocene (DMFc) located in 1,2-dichloroethane (DCE) functions as the reductant, the adjacent aqueous phase containing sulfuric acid provides the proton, and the polarization of the interface can be controlled either externally by a voltage or chemically by the distribution of different salts with a common ion. The main advantage of this biphasic system is that the oxygen reduction by DMFc can be stopped at the formation of H_2O_2. The resulting concentration of H_2O_2 has been measured and shows a yield of 20% with respect to the concentration of the reducing agent (DMFc). Moreover, the reaction could be catalyzed by Cobalt(II) 5-(*o*-aminophenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin featuring a stong proton complexation and interfacial affinity. In summary, this work illustrates how a biphasic system can be used to simultaneously supply electrons from nonaqueous donors and protons from an aqueous phase to drive interfacial reactions.

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Physical Chemistry **446**

Vibrational Predissociation via Isomerisation: The Photodissociation of Nitrosamine in the S_1 State.

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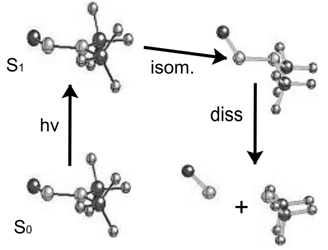
Two instructive cases of vibrational predissociation [1] previously studied in our laboratory are methylnitrite [2] (MN) and N,N-dimethylnitrosamine (DMN) [3, 4]. While MN can be considered a classical case , DMN ($(CH_3)_2N–NO$) has been proposed a very special predissociation involving large amplitude motions with structural changes prior to the bond cleavage. The present study reports the result of a reinvestigation of the mechanistic features of DMN predissociation which supports the earlier proposal of Persico, Cacelli and Ferretti [5]. Using ab initio MCSCF we calculated the S_1 PES along the N=O (stretch) and N–N (dissociation) coordinates for the planar and its isomeric structures (see Figure). The result of our calculations including the S_1 PES, the $S_0 \longrightarrow S_1$ ($n\pi^*$)) absorption spectrum and the vertical excitation energies show that S_1 nitrosamine cannot dissociate keeping its planar structure. Only after a rapid and barrierless transformation to the isomeric form (pyramidalized and twisted) dissociation to $(CH_3)_2N$ + NO can occur.



The entire process proceeds on a subpicosecond time scale as also manifested by the non–Boltzmann vibrational and rotational state distributions of NO and the angular momentum and recoil velocity anisotropy of the fragments [3].

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Physical Chemistry **447**

Elucidating the particle-size effect of oxide-supported palladium nanoparticles on the mechanism of hydride formation

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Palladium is a versatile hydrogenation catalyst because of its ability to dissociate and dissolve hydrogen, which also leads to hydride formation [1]. To understand the particle size effect in hydrogenation, we studied the structure and formation of the hydrides. Oxide-supported palladium nanoparticles of 13, 28, and 105 Å were synthesized by incipient-wetness impregnation. These particles were reduced and their interaction with hydrogen at room temperature was studied using in situ x-ray absorption spectroscopy. Hydride formation was observed by lattice expansion and the formation of characteristic spectral features caused by the new Pd-H antibonding state [2]. The L_3-edge spectra were reproduced using full multiple scattering analysis and density of state (DOS) calculations [3], and the contribution of interstitial and surface hydrogen to the new Pd-H antibonding state could be distinguished. The particle size strongly affected the hydride formation. However, even the smallest particles had interstitial hydrogen and thus formed some type of hydride.

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Physical Chemistry **448**

Conformational Behavior of Cinchonidine Revisited: A Combined Theoretical and NOESY Study

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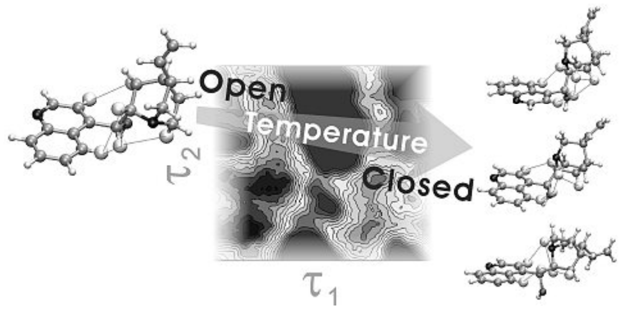
The unique combination of the stereogenic centers of cinchona alkaloids is beneficially exploited to obtain optically pure compounds by chiral separation, homogeneous, and heterogeneous catalysis. Understanding of their rich conformational behavior plays a key role in further improvements of those processes. In this work, conformational space of cinchonidine has been explored by means of ab initio potential and free energy surfaces and the temperature-induced changes of conformational populations were studied by a combined NOESY-DFT analysis. The DFT derived potential energy surface investigation identified four new conformers. Among them, Closed(7) is substantially relevant to fully understand the conformational behavior. The energy surfaces gave access to the favored transformation pathways at different temperatures (280-320K). They also revealed the reasons for the negligible presence of energetically stable conformers and explained the experimentally observed temperature dependence of the populations.



Physical Chemistry **449**

Stability of Pd-based catalysts prepared by flame-spray pyrolysis

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Palladium-based catalysts belong to the most efficient catalysts for several combustion reactions. Although still under debate, the most active form is considered to be a combination of Pd and PdO or pure PdO [1]. Palladium oxide however has a limited thermal stability, decomposing at between 600-700°C in pure helium or at higher temperature with higher oxygen partial pressure. This property greatly reduces the activity of these catalysts between 600 and 800°C [2].

Recent research on Rh-based hydrogenation catalysts prepared by flame-spray pyrolysis (FSP) revealed the presence of a large amount of cationic rhodium species, along with a higher resistance to reduction compared with commercial catalysts [3]. This finding prompted us to investigate the thermal stability and activity of palladium based catalysts prepared by FSP. Several supports were used to study their effect on the stability of the PdO and the overall catalytic activity, including non-reducible supports (Al_2O_3, SiO_2 and $MgAl_2O_4$) as well as reducible supports (TiO_2, ZrO_2 and CeO_2).

The catalysts were used for the catalytic combustion of methane and characterized by nitrogen adsorption (BET), XRD, thermogravimetry and Raman spectroscopy. Preliminary results from these experiments indicate that especially the thermal stability of the support plays a crucial role in conserving the catalytic activity.

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Physical Chemistry **451**

Parallel two channel near and far field fluorescence microscopy

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A new two channel fluorescence microscopy technique for surface-generated fluorescence is presented. The realized fluorescence microscope allows high resolution imaging of aqueous biological samples. The core element of the instrument is a parabolic mirror objective used to collect the fluorescence emission at large surface angles above the critical angle of the water/glass interface. An aspheric lens, incorporated into the solid parabolic element, is used for diffraction limited laser focusing and for collecting fluorescence at low angles with respect to the optical axis. By separated collection of the fluorescence emitted into supercritical and subcritical angles, two detection volumes strongly differing in their axial resolution are generated at the water/glass interface. Consequently, the signals from surface-bound and unbound diffusing fluorescent molecules can be obtained simultaneously. Unlike in total internal reflection microscopy, the parabolic mirror objective easily achieves a diffraction limited excitation/detection volume at the water/glass interface. An excellent signal-to-background ratio at moderate illumination intensity, diffraction limited resolution, radical reduction of the detection volume along the optical axis, easy handling and stability, make the two channel fluorescence microscope a powerful technique for surface fluorescence measurements.

Physical Chemistry **450**

Rovibrational structure of the low-lying electronic states of Xe_2^+ by PFI-ZEKE photoelectron spectroscopy

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Pulsed-field-ionization zero-kinetic-energy photoelectron spectra of Xe_2^+ have been measured in the range between 91 000 cm^{-1} and 107 200 cm^{-1}, where the lowest electronic states of the cation are located. Using a two-photon excitation scheme via selected rovibrational levels of the C 0_u^+ intermediate state, it was possible for the first time to observe the rotational structure of several vibrational bands of the I (1/2u), I (3/2u), I (3/2g) and II (1/2u) electronic states. For the ground ionic state I (1/2u) even the Ω-doubling was resolved. Analysis of the experimental data allows us to extract accurate values for the rotational and Ω-doubling constants. These constants are used to test several sets of potential energy functions for the six low-lying electronic states of Xe_2^+ available in the literature.

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Physical Chemistry **452**

SLOW SAMPLES OF COLD RADICALS BY MULTISTAGE ZEEMAN DECELERATION

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With the goals of: (i) performing ultra-high resolution spectroscopy with long interaction times between a cloud of cold atoms or molecules and a narrow bandwidth radiation field, and (ii) studying cold reactive collisions in which the kinetic energies and quantum states of the colliding particles may be controlled to a high degree, a multistage Zeeman decelerator for neutral radicals has recently been developed in our laboratory [1,2].

The results of a recent series of experiments in which we have decelerated ground state H and D atoms will be presented. In these experiments magnetic fields of 1-2 T were pulsed in each coil for tens of microseconds, with rise and fall times shorter than 5 μs. With this instrument we have been able to produce slow beams (velocities below 100 ms^{-1}) of translationally cold (temperature of ∼30 mK) H atoms [3]. The atoms are detected by photoionization and the velocity distribution of the decelerated atom cloud was determined by measuring the time-of-flight distribution of the H^+ ions. Magnetic reflection and trapping at the end of the decelerator can be performed.

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doi:10.2533/chimia.2008.671 CHIMIA **2008**, *62*, No. 7/8

Physical Chemistry **453**

Beyond nature: a surface that resists wetting by water and oils

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Inspired by nature, many artificial surfaces have been developed in the last decade that mimic the so called Lotus Effect® [1]. On such so called superhydrophobic surfaces, drops of water remain almost spherical and easily roll off. Unknown in nature is a similar effect for oils. In fact, all natural and most artificial superhydrophobic surfaces face the problem of oily contamination. We have recently developed a coating [2] which, applied to textiles, results in fabrics that are completely non wettable by both water and oils. Even drops of non polar liquids with surface tensions below 30mN/m roll off these surfaces on slight inclination. To date, such surfaces are extremely rare and previously required complicated coating procedures or intricate surface manufacturing [3].

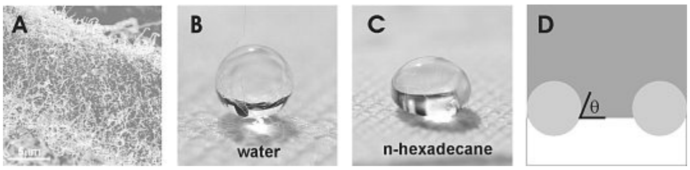

Figure 1. A: A polyester (PET) fiber coated with fluorosilane modified silicone nanofilaments (FSN). B/C: A drop of water/hexadecane on a PET fabric coated with FSN. D: Due to their special surface geometry, fibrous structures are able to resist wetting even though θ < 90° (adapted from [3])

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Physical Chemistry **454**

Corannulene on Cu(111) surface structure and properties using a first-principle theoretical approach

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The interaction of curved aromatic carbon surfaces with metal atoms represents an area of broad interest in organometallic chemistry. The intriguing question regarding the preference for metal binding to the concave versus convex side has been investigated both theoretically and experimentally, most notably focusing on Corannulene $C_{20}H_{10}$ (COR) [1] as prototype system. In this work, we study the specific case of COR adsorption on Cu(111) surface. The interest in this system stems from recent STM experimental findings, [2] which show that CORs adsorbed on Cu(111) gives rise to very peculiar supramolecular aggregation processes. In order to elucidate the fundamental mechanism involved, we adopt a first-principle electronic structure approach by adding to a standard DFT-GGA framework a semiempirical term taking into account dispersion contributions [3], employing the SIESTA code [4]. Structural relaxations of a single COR molecule located on top of the high symmetry sites of a six-layer Cu(111) slab are performed. Subsequently, electronic structure analysis is performed based on projected density of states (PDOS) and work function modification, upon molecule adsorption. Investigations of the Cu(100) slab are also of interest. Ultimately, we will extend structural analysis to the case of several molecules on the copper substrate so to distinguish the contributions of molecule-substrate interaction and molecule-molecule interaction to the adsorption mechanism.

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Polymer Science **455**

Soft Nanotechnology - from Colloid Chemistry to Nanostructured Functional Materials

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I will demonstrate how we can tune the size, shape, surface functionality and properties of nanoparticles and use them as ideal model systems for fundamental investigations as well as for materials applications. These particles can be used in order to study the equilibrium and non-equilibrium phase behavior of colloidal suspensions with different interaction potentials, and I will demonstrate how they allow us to investigate various phase transitions such as crystallization or gel and glass formation. While different nanoparticles are vital for fundamental studies of soft condensed matter, they also offer fascinating possibilities in materials science, and I will thus also demonstrate how we can create nanostructured materials with novel properties using functionalized and responsive particles.

Polymer Science **456**

Electrostatic Interactions between Colloidal Particles Covered with Oppositely Charged Dendrimers

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The colloidal probe technique, based on the atomic force microscope (AFM), is used to measure interaction forces between sulfate polystyrene latex particles covered with poly(amidoamine) (PAMAM) dendrimers, with different coverage, ionic strength and dendrimer generation. When increasing the adsorbed amount of dendrimer, the overall charge can be tuned from negative to positive values, through the isoelectric point (IEP). The potentials obtained from the direct force measurements between the colloidal particles agree well with the ones measured with electrophoresis. At the IEP, a long-range attraction is measured. Ionic strength and dendrimer generation influence the range of this interaction. The attractive force can be explained by the surface charge heterogeneities resulting from the lateral distribution of positively charged dendrimers onto negatively charged particles.