

Fachverband Molekülphysik (MO)

Karl Kleinermanns
 Institut für Physikalische Chemie
 Lehrstuhl für Molekülspektroskopie und Nanosysteme
 Universitätsstr. 26.43.02
 40225 Düsseldorf
 kleinermanns@uni-duesseldorf.de

Übersicht der Hauptvorträge und Fachsitzungen

(Hörsäle 3F und 3G; Poster C1)

Hauptvorträge

MO 1.1	Mo	14:00–14:30	3F	Ultrafast Dynamics of Non-Radiative Processes in Electronically Excited DNA Building Blocks — ●FRIEDRICH TEMPS, NINA K. SCHWALB
MO 3.1	Mo	14:00–14:30	3G	Dynamics and Mobility of Electronic Excitations in Organic Materials — ●STEFAN LOCHBRUNNER
MO 5.1	Di	8:30– 9:00	3F	The Photochemistry of N-Oxides - A White Spot in Femtosecond Spectroscopy — THORBEN CORDES, NADJA REGNER, ELINA BORYSOVA, BJÖRN HEINZ, ●PETER GILCH
MO 8.1	Di	8:30– 9:00	3G	Cold Polar Molecules: From Production to State-Selective Detection — ●PEPIJN W.H. PINKSE, LAURENS D. VAN BUUREN, MICHAEL MOTSCH, MARKUS SCHENK, CHRISTIAN SOMMER, MARTIN ZEPPENFELD, GERHARD REMPE
MO 12.1	Do	8:30– 9:00	3F	Reactions of negative ions at low energy — JOCHEN MIKOSCH, SEBASTIAN TRIPPEL, RICO OTTO, CHRISTOPH EICHHORN, PETR HLAVENKA, MATTHIAS WEIDEMÜLLER, ●ROLAND WESTER

Fachsitzungen

MO 1.1–1.7	Mo	14:00–16:00	3F	Biomoleküle
MO 2.1–2.10	Mo	16:30–19:00	3F	Elektronische Spektroskopie
MO 3.1–3.7	Mo	14:00–16:00	3G	Femtosekundenspektroskopie I
MO 4.1–4.10	Mo	16:30–19:00	3G	Femtosekundenspektroskopie II
MO 5.1–5.7	Di	8:30–10:30	3F	Photochemie I
MO 6.1–6.8	Di	11:00–13:00	3F	Photochemie II
MO 7.1–7.8	Di	14:00–16:00	3F	Quantenkontrolle
MO 8.1–8.7	Di	8:30–10:30	3G	Kalte Moleküle I (gemeinsam mit Q)
MO 9.1–9.8	Di	11:00–13:00	3G	Kalte Moleküle II (gemeinsam mit Q)
MO 10.1–10.8	Di	14:00–16:00	3G	Kalte Moleküle III (gemeinsam mit Q)
MO 11.1–11.6	Di	16:30–18:00	3G	Ultrakalte Moleküle (gemeinsam mit Q)
MO 12.1–12.7	Do	8:30–10:30	3F	Stossprozesse, Energietransfer I (gemeinsam mit A)
MO 13.1–13.4	Do	11:00–12:15	3F	Stossprozesse, Energietransfer II (gemeinsam mit A)
MO 14.1–14.8	Do	8:30–10:30	3G	Cluster
MO 15.1–15.5	Do	11:00–12:15	3G	Experimentelle Techniken
MO 16.1–16.11	Di	14:00–19:00	Poster C1	Biomoleküle
MO 17.1–17.8	Di	14:00–19:00	Poster C1	Elektronische Spektroskopie
MO 18.1–18.12	Di	14:00–19:00	Poster C1	Femtosekundenspektroskopie
MO 19.1–19.1	Do	16:30–19:00	Poster C1	Photochemie
MO 20.1–20.4	Do	16:30–19:00	Poster C1	Quantenkontrolle
MO 21.1–21.7	Do	16:30–19:00	Poster C1	Stossprozesse, Energietransfer
MO 22.1–22.5	Do	16:30–19:00	Poster C1	Theorie: Quantenchemie und Moleküldynamik
MO 23.1–23.4	Do	16:30–19:00	Poster C1	Experimentelle Techniken
MO 24.1–24.8	Do	16:30–19:00	Poster C1	Kalte Moleküle
MO 25.1–25.6	Do	16:30–19:00	Poster C1	Cluster
MO 26.1–26.5	Do	16:30–19:00	Poster C1	Spektroskopie in He-Tröpfchen

Mitgliederversammlung des Fachverbands Molekülphysik

Mittwoch, 12.3. 13:00 Hörsaal 3G

- Bericht
- Planung der nächsten Tagungen (u.a. Symposien 2009)
- Sonstiges, Wünsche und Anregungen

MO 1: Biomoleküle

Zeit: Montag 14:00–16:00

Raum: 3F

Hauptvortrag MO 1.1 Mo 14:00 3F
Ultrafast Dynamics of Non-Radiative Processes in Electronically Excited DNA Building Blocks — ●FRIEDRICH TEMPS and NINA K. SCHWALB — Institut für Physikalische Chemie, Universität Kiel, D-24098 Kiel

In a thrust to shed light on the mechanisms responsible for the high UV photostability of DNA, we study the electronic relaxation dynamics of free nucleobases, selected hydrogen-bonded base pairs, and short single- and double-stranded oligonucleotides using femtosecond fluorescence spectroscopy. Recent new results concern the modified base N^6N^6 -dimethyladenine, which shows so-called “dual fluorescence”. Time-resolved measurements after excitation at different wavelength, starting just above the electronic origin, showed that the observed red-shifted emission previously ascribed to an intramolecular charge transfer state arises virtually without time delay. By comparison with adenine, it is suggested that the optically excited state undergoes a transformation through a conical intersection to a relaxed excited state, which is responsible for the red fluorescence and may be related to the $\pi\pi^*(L_b)$ or the $n\pi^*$ state. In addition, time-resolved fluorescence decay data will be reported for guanosine-cytidine (G:C) Watson-Crick base pairs in solution. The results demonstrate a strong acceleration of the radiationless electronic relaxation in G:C compared to the free monomers. Excitation wavelength and solvent dependent measurements resolved the gas vs. solution phase puzzle, where apparently different behaviors were observed. Eventually, an outlook is given on experiments on short DNA chains with different sequences.

MO 1.2 Mo 14:30 3F
Structural Assignment of Adenine Aggregates in $CDCl_3$ — ●LARS BIEMANN¹, THOMAS HÄBER¹, DANIELA MAYDT², KLAUS SCHAPER², and KARL KLEINERMANN¹ — ¹Institut für Physikalische Chemie, Heinrich-Heine Universität Düsseldorf, 40225 Düsseldorf, Germany — ²Institut für Organische Chemie, Heinrich-Heine Universität Düsseldorf, 40225 Düsseldorf, Germany

We reinvestigated the self-association of 9-substituted adenine derivatives in $CDCl_3$ solutions and present the infrared spectra of 9-ethyladenine and N-methyl-9-ethyladenine and its aggregates in the spectral regions between 1500 and 1800 cm^{-1} and between 2700 and 3600 cm^{-1} . Wavelength dependent absolute extinction coefficients of the monomer and dimers are presented on the basis of a simple deconvolution method. Comparison of the deconvoluted dimer spectra with quantum chemical calculations allows for a structural assignment of the two dimer structures that coexist in 9-ethyladenine/ $CDCl_3$ solutions. In contrast, the dimer spectrum of N-methyl-9-ethyladenine is dominated by a single isomer.

MO 1.3 Mo 14:45 3F
IR/UV-double resonance spectroscopy of 3-hydroxyflavone and its aggregates with water — ●KRISTINA BARTL, ANDREAS FUNK, HOLGER FRICKE, KIRSTEN SCHWING, and MARKUS GERHARDS — TU Kaiserslautern, Fachbereich Chemie, Schrödingerstr. 52, 67663 Kaiserslautern & H.-Heine Uni Düsseldorf, Institut für Physikalische Chemie I, 40225 Düsseldorf

Flavonoids are well known for their antioxidative and photoprotective effects. Spectroscopically 3-hydroxyflavone is of special interest, as a keto-enol-tautomerism takes place after electronic excitation. In order to obtain structural information about 3-hydroxyflavone and its aggregates with water, IR laser spectroscopy from the fingerprint region to the OH stretching modes is a very powerful tool especially in combination with UV spectroscopy and mass spectrometry leading to the isomer selective IR/R2PI [infrared/ resonant 2-photon ionisation] method. We show that the application of this method to the electronically excited states yield in combination with ab initio calculations direct information on the structure and reaction coordinates. For the aggregates with water different isomers have to be considered and it is the strength of this technique that a structure can unambiguously be assigned according to the IR spectra of the excited states. Thus we are able to answer the open question if proton transfer takes place in the aggregates after electronic excitation.

MO 1.4 Mo 15:00 3F
Investigation of Optically “Dark” Excited States of

Carotenoids by Femtosecond Two-Photon Excitation Spectroscopy — ●ALEXANDER BETKE¹, BERND VOIGT¹, HEIKO LOKSTEIN², and RALF MENZEL¹ — ¹Institut für Physik/Photonik, Universität Potsdam, Am Neuen Palais 10, D-14415 Potsdam, Germany — ²Institut für Biochemie und Biologie, Universität Potsdam, Karl-Liebknecht-Str. 24-25, D-14476 Potsdam-Golm, Germany

Carotenoids are essential components of pigment-protein-complexes in photosynthetic organisms: they are important for structural stability, serve as accessory light-harvesting pigments and protect the photosynthetic apparatus from photo-oxidative damage. The carotenoid lowest excited singlet state S_1 ($2^1A_g^-$) is assumed to be relevant for the latter two functions. For a study of the underlying mechanisms a proper knowledge of its energetic position would be necessary. However, single photon transitions between the carotenoid ground state S_0 ($1^1A_g^-$) and this state are symmetry-forbidden and thus, its investigation by conventional spectroscopy is hampered. On the other hand the S_0 - S_1 -transition is two-photon allowed, which makes two-photon absorption a suitable approach for an investigation of the carotenoid S_1 energies. We present near-infrared femtosecond laser two-photon excitation spectra of light-harvesting antenna-complexes with different carotenoid complements and discuss implications for excitation energy transfer and photoprotective mechanisms.

This research is supported by the DFG (SFB 429, TP A2).

MO 1.5 Mo 15:15 3F
Comparison of the fluorescence kinetics of detergent-solubilized and membrane-reconstituted LH2 complexes — ●TOBIAS PFLOCK¹, MANUELA DEZI², GIOVANNI VENTUROLI², RICHARD J. COGDELL³, JÜRGEN KÖHLER¹, and SILKE OELLERICH¹ — ¹Experimentalphysik IV, Universität Bayreuth, D-95447 Bayreuth — ²Dept. of Biology, University of Bologna, Italy — ³GBRC, University of Glasgow, UK

Picosecond time-resolved fluorescence spectroscopy has been used in order to compare the fluorescence kinetics of detergent-solubilized and membrane-reconstituted light-harvesting 2 (LH2) complexes from the bacteria *Rhodospseudomonas* (Rps.) acidophila and *Rhodobacter* (Rb.) sphaeroides. LH2 complexes were reconstituted in phospholipid model membranes at different lipid:protein-ratios and all samples were studied exciting with a wide range of excitation densities. While the detergent-solubilized LH2 complexes from Rps. acidophila showed monoexponential decay kinetics ($\tau_f = 980$ ps) for excitation densities of up to $3 \cdot 10^{13}$ photons/(pulse· cm^2), the membrane-reconstituted LH2 complexes showed multiexponential kinetics even at low excitation densities and high lipid:protein-ratios. The latter finding indicates an efficient clustering of LH2 complexes in the phospholipid membranes. Similar results were obtained for the LH2 complexes from Rb. sphaeroides.

MO 1.6 Mo 15:30 3F
Raman Spectroscopic Investigation of the Influence of Biological Rhythms on Bone Composition of Hamsters — ●JING SHEN^{1,2}, JIMING HU², ALEXANDER LERCHL¹, and ARNULF MATERNY¹ — ¹Jacobs University Bremen, Germany — ²Wuhan University, China

Biological rhythms regulate the lives of mammals. It has been reported that changes of the photoperiod result in variations of the melatonin synthesis and sequential changes of body weight, fur color and gonadal function in Djungarian hamsters [1]. Since the hormone level acts as a regulator for the metabolism of bone, certain changes in the bone composition have to be expected. In our study, Raman spectroscopy was applied to observe the differences in bones comparing long- (16L:8D) and short-day (8L:16D) photoperiod Djungarian hamsters. Recently, Raman spectroscopy has been widely used in biology and medicine due to its capability to analyze different bio-components. The method provides information about inorganic component-calcium compounds and organic component-collagen in bone at the same time. Our results show that LD cortical bone samples possess a higher phosphate-to-carbonate ratio in both femur and tibia. It is assumed that the metabolism of the bone is influenced by hormones such as gonadotrophin and melatonin, which are produced in varying amounts during the different photoperiods.

[1] A. Lerchl *et al.*, *Neuroendocrinology* **57**,359 (1993).

MO 1.7 Mo 15:45 3F

Raman Spectroscopy for the Characterization of Animal Tissue — Toward Molecular Monitoring of Tumorigenicity and Hormonal Changes — ●PATRICE DONFACK¹, JING SHEN^{1,2}, ALEXANDER LERCHL¹, and ARNULF MATERNY¹ — ¹Jacobs University Bremen, Germany — ²Wuhan University, China

Current investigation methods of biological systems are mostly based on time-demanding immunoassays and histopathological examination of sample biopsies. The availability of rapid *in-situ* techniques would be of great advantage. A potential candidate is Raman spectroscopy (RS), which provides specific molecular fingerprints in a non-invasive and non-destructive way. In our contribution we present two examples for an application of RS for the investigation of animal tissue.

(i) Hamsters are strongly influenced by seasonal changes of day and night ratio. Experiments on metabolic or hormonal changes in hamsters unequally exposed to daylight have resulted in changes in the Raman spectra of spleen and liver tissue. (ii) RS was also performed to characterize biomolecular alterations in cells of AKR mice predisposed to leukemia. The Raman spectra of AKR mice spleen tissues show a prominent contribution of the β -sheet conformation, which can be unambiguously assigned to the protein's amide I band. The intensity ratios of this amide I band and the CH₂-deformation line at 1450 cm⁻¹ was found to be different for cancerous and healthy mice. Clear changes could also be observed for the nucleic acid band at approx. 1085 cm⁻¹ and *e.g.* for a double band at 1606 and 1635 cm⁻¹.

MO 2: Elektronische Spektroskopie

Zeit: Montag 16:30–19:00

Raum: 3F

MO 2.1 Mo 16:30 3F

State-dependent gerade/ungerade intensity ratios in the Auger spectrum of N₂ — ●RALPH PÜTTNER^{1,2}, HIRONOBU FUKUZAWA², XIAO-JING LIU², SERGEY SEMENOV³, NIKOLAI CHEREPKOV³, TAKAHIRO TANAKA⁴, MASAMITSU HOSHINO⁴, HIROSHI TANAKA⁴, and KIYOSHI UEDA² — ¹Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, D-14195 Berlin-Dahlem, Germany — ²Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan — ³State University of Aerospace Instrumentation, 190000, St. Petersburg, Russia — ⁴Department of Physics, Sophia University, Tokyo 102-8554, Japan

Auger spectra of the N $1s_{g,u}$ core holes in N₂ to five different quasi-stable final states are presented; they exhibit the gerade/ungerade splitting as well as vibrational progressions. The N $1s_{g,u}$ /N $1s_u$ Auger intensity ratio depends on the final state. In particular, for the states X $^1\Sigma_g^+$ and D $^1\Sigma_u^+$ ratios of $\cong 2.1$ and $\cong 0.8$ are derived. These values are in agreement with *ab initio* calculations and the large value for the X state can qualitatively be related to the gerade or ungerade symmetry of the Auger electron. In addition, from the vibrational progressions in the Auger spectrum, the vibrational energies $\hbar\omega$, the anharmonicities $x\hbar\omega$ and the equilibrium distances R_e for the dicationic final states are derived in a fit analysis assuming Morse potentials.

MO 2.2 Mo 16:45 3F

Vibrationally resolved C $1s^{-1}$ Auger spectrum of CO₂ — ●VLADIMIR SEKUSHIN¹, RALPH PÜTTNER^{1,2}, GÜNTER KAINDL¹, XIAO-JING LIU², HIRONOBU FUKUZAWA², KIYOSHI UEDA², TAKAHIRO TANAKA³, MASAMITSU HOSHINO³, and HIROSHI TANAKA³ — ¹Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany — ²Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan — ³Department of Physics, Sophia University, Tokyo 102-8554, Japan

The high-resolution Auger spectrum of CO₂ subsequent to C $1s^{-1}$ photoionization is reported along with the corresponding photoelectron spectrum. Auger transitions to seven quasi-stable final states are observed. They are assigned on the basis of theoretical results in combination with the assumption that the Auger spectrum is dominated by transitions to singlet states. From a Franck-Condon fit analysis of the vibrational progressions in the Auger spectrum, the vibrational energies $\hbar\omega$, the anharmonicities $x\hbar\omega$ and the equilibrium distances R_e for the dicationic final states are derived assuming Morse potentials. The relative intensities of the various C $1s^{-1}$ Auger transitions are also obtained.

MO 2.3 Mo 17:00 3F

Angle sensitive Doppler-spectroscopy of inversion symmetric molecules — ●RAINER HENTGES¹, AXEL REINKÖSTER¹, MARKUS BRAUNE¹, SANJA KORICA¹, BURKHARD LANGER², OLIVER KUGELER³, UWE HERGENHAHN⁴, and UWE BECKER¹ — ¹Fritz-Haber-Institut der MPG, Berlin — ²Freie Universität Berlin — ³BESSY GmbH, Berlin — ⁴MPI für Plasmaphysik, Garching

One of the most intriguing effects of quantum mechanics is the tunneling and over the barrier reflection effect. Electron tunneling is the basis of the separation of the parity eigenstates in all homonuclear diatomic or, more general, inversion symmetric molecules. However, electron tunneling on real time scale became only very recently subject of experimental investigations. These investigations were still limited

to tunneling barriers induced by the probe pulse. Natural barriers, such as the barriers between the two identical atoms in homonuclear molecules, have so far never been studied. We present the first results of indirect time resolved studies on the electron tunneling effect in O₂ and SF₆. Excitation of these molecules into dissociative excited states gives rise to autoionization of the dissociating system [1]. The fingerprint of this process is the Doppler-shift of the autoionizing electrons in the molecular frame. We show that the Doppler-shifted autoionizing lines provide a tool to study the fraction of core-holes which have been tunneled to the other atomic site of the homonuclear molecule during the deexcitation process. This is an indirect measurement of electron tunneling in homonuclear molecules.

[1] Björneholm et al., Phys. Rev. Lett. 84, 2826 (2000)

MO 2.4 Mo 17:15 3F

Interference effects in the photoelectron emission of inversion symmetric molecules — ●SANJA KORICA¹, AXEL REINKÖSTER¹, MARKUS BRAUNE¹, RAINER HENTGES¹, BURKHARD LANGER², and UWE BECKER¹ — ¹Fritz-Haber-Institut der MPG, Berlin — ²Freie Universität Berlin

Inversion symmetric molecules generate eigenstates of the parity operator. These gerade and ungerade called eigenstates reflect the phase coupling between the atomic sites of the molecule, being either positive or negative. Photoelectron emission from these molecules gives rise to oscillating partial cross sections with a phase shift of π from these symmetry eigenstates. The oscillation period depends on the bond lengths of the corresponding molecules. Cohen and Fano [1] were the first who mentioned and analysed this phenomenon of wave like behavior of photoelectron emission. Regarding the de Broglie wavelengths of the emitted photoelectron there could be less than one period up to more than ten periods of oscillation depending on the photon energy range available for experimental investigations. We show that the study of the Cohen-Fano oscillations from molecular hydrogen to the bucky ball molecule C₆₀ covers two orders of magnitude in oscillation periods. This shows that the Cohen-Fano model of wavelike emission for two indistinguishable emitter sites is an universal model.

[1] H. D. Cohen and U. Fano, Phys. Rev. 150, 30 (1966)

MO 2.5 Mo 17:30 3F

Time-resolved photoelectron spectroscopy of DNA base clusters — ●THOMAS SCHULTZ¹, ELENA SAMOYLOVA¹, YULIYA RULYK¹, HANS-HERMAN RITZE¹, WOLFGANG RADLOFF¹, and INGOLF VOLKER HERTEL^{1,2} — ¹Max-Born Institut Berlin, Max-Born-Strasse 2A, 12489 Berlin — ²Fachbereich Physik der Freien Universität Berlin, Arnimallee 14, 14195 Berlin

The photochemistry of large molecules can be due to inherent properties of the light-absorbing chromophores, but can also be dominated by intermolecular interactions. The latter play a very important role in biological systems, where well defined structure often determines molecular function. We investigate the photochemistry, and in particular the photostability, of DNA building blocks in vacuo and try to reproduce structural features in small molecular clusters. Reaction and relaxation pathways can be mapped in real time by time-resolved pump-probe ionization and coincident detection of electrons and ions.

MO 2.6 Mo 17:45 3F

Transfer processes in organic donor-acceptor dyads con-

taining tetraphenylbenzidine and perylenebisimide studied by time-resolved spectroscopy — ●CHRISTIANE HOFMANN¹, PETER BAUER², MUKUNDAN THELAKKAT², and JÜRGEN KÖHLER¹ — ¹Department of Experimental Physics IV and BIMF, University of Bayreuth, D-95440 Bayreuth, Germany — ²Applied Functional Polymers, University of Bayreuth, D-95440 Bayreuth, Germany

We investigated transfer processes in organic donor-acceptor dyads by time-resolved fluorescence spectroscopy. In the dyads, perylenebisimide (PBI) is covalently linked to a tetraphenylbenzidine (TPD) unit by a spacer. TPD acts as an energy transfer donor, PBI as an acceptor. Fluorescence lifetimes of both TPD and PBI have been determined for three different types of spacer and as a function of the solvent. We found that changing the spacer length had a significant influence on the TPD lifetime and on energy transfer efficiency. For all three TPD-PBI dyads the PBI lifetimes were considerably shorter than those measured for pure PBI and varied significantly upon changing the chemical composition of the spacer. We could also show that the PBI lifetimes depend noticeably on the solvent. Particularly, we found a correlation between the acceptor decay rate and the rotational diffusion time constant, which in turn is a function of the local viscosity of the solvent.

MO 2.7 Mo 18:00 3F

The structure of cyclic azaindole-water clusters from rotationally resolved electronic spectroscopy — ●MICHAEL SCHMITT¹, THI BAO CHAU VU¹, YURIY SVARTSOV¹, W. LEO MEERTS², and IVO KALKMAN² — ¹Heinrich-Heine-Universität Düsseldorf, Institut für Physikalische Chemie — ²Department of Molecular and Laser Physics, Institute for Molecules and Materials, Radboud University Nijmegen

Azaindole has two possible sites for hydrogen bonding, one potentially acting as proton donor, the other as proton acceptor. This behaviour, which is shared with chromophores like 2-pyridone and 7-hydroxyquinoline opens the possibility to form chains of water molecules bridging the two binding sites. Since azaindole may exist in two tautomeric forms, 1*H*-7-azaindole (1*H*-pyrrolo[2,3-*b*]pyridine) and 7*H*-7-azaindole (7*H*-pyrrolo[2,3-*b*]pyridine) these water chains may be capable of inducing a proton transfer which interconverts the two tautomeric forms. The barriers for this proton transfer depend strongly on the number of water molecules in the chain and on the electronic state. In the talk we present our latest results on the structure and tunneling motions in the water clusters of azaindole from a comparison of rotationally resolved electronic spectroscopy to ab initio calculations.

MO 2.8 Mo 18:15 3F

High resolution spectroscopy of neurotransmitter analogues: tryptamine and 5-methoxytryptamine — ●THI BAO CHAU VU, MARCEL BÖHM, and MICHAEL SCHMITT — Heinrich-Heine-Universität Düsseldorf, Institut für Physikalische Chemie

The activity of biomolecules depends strongly on their structure. In case of different conformers of neurotransmitters like serotonin or melatonin

the questions arises which is the most stable one in aqueous solution. We investigated the structure and conformational stabilization of microsolvated complexes of tryptamine and 5-methoxytryptamine, the building blocks of the above neurotransmitters by rotationally resolved electronic spectroscopy. In the present talk the results of these experiments will be presented and compared to the results of ab initio calculations.

MO 2.9 Mo 18:30 3F

Rotationally resolved electronic spectroscopy of the benzoic acid dimer — ●MICHAEL SCHMITT¹, THI BAO CHAU VU¹, W. LEO MEERTS², and IVO KALKMAN² — ¹Heinrich-Heine-Universität Düsseldorf, Institut für Physikalische Chemie — ²Department of Molecular and Laser Physics, Institute for Molecules and Materials, Radboud University Nijmegen

The assignment and simulation of rotationally resolved electronic spectra gets more and more complicated with increasing molecule size, due to strongly overlapping transitions. Many automated fitting techniques for extraction of the molecular parameters from the spectra have often the disadvantage of being trapped in local minima. The use of genetic algorithms for fitting of the parameters in combination with a cost function for the fit, that allows for determination of similarities between experiment and simulation solves most of the above problems. The genetic algorithms show their full power with increasing complexity of the spectra and number of parameters to be fit. In the present talk I will present the application of the method to the interpretation of the rovibronic spectra of the benzoic acid dimer. The molecular structure in both electronic states as well as the H-bond tunneling dynamics will be discussed and compared to other homodimers, like the formic acid dimer.

MO 2.10 Mo 18:45 3F

Detection of dark states of porphyrins — ●ANDREAS-NEIL UNTERREINER¹, OLIVER SCHALK¹, HELGE BRANDS¹, and SILVIU BALABAN² — ¹Universität Karlsruhe (TH), Lehrstuhl für Molekulare Physikalische Chemie, 76128 Karlsruhe — ²Forschungszentrum Karlsruhe, Institut für Nanotechnologie, 76021 Karlsruhe

Porphyrins are known to exhibit two absorbing bands, the B-band in the visible (500-650 nm) and the Soret-band in the UV (420 nm). In order to explain ultrafast dynamics after excitation to the Soret band, dark states in its vicinity have been postulated. Here, we present the first direct observation of these states in 5,10,15,20-tetra-*p*-tolyl-21*H*,23*H*-porphyrin (TTP-H₂) and 5,10,15,20-tetra-*p*-tolyl-porphyrinato zinc II (ZnTTP) by means of pump-probe and transient anisotropy experiments. After excitation to the Q-band, the molecules were probed by NIR-pulses in the range between 950 and 1350 nm in order to study states of gerade-symmetry. Examination of transient spectra and anisotropy revealed the energies of the two lowest so called dark states. The experimental results are compared with predictions from theoretical calculations.

MO 3: Femtosekundenspektroskopie I

Zeit: Montag 14:00–16:00

Raum: 3G

Hauptvortrag MO 3.1 Mo 14:00 3G
Dynamics and Mobility of Electronic Excitations in Organic Materials — ●STEFAN LOCHBRUNNER — Institut für Physik, Universität Rostock, Universitätsplatz 3, 18055 Rostock

In organic materials and thin layer systems designed for optoelectronics applications complex energy transport and electronic relaxation processes govern the performance. Since many of them contribute it is difficult to derive a microscopic understanding purely from measuring device parameters. Femtosecond spectroscopy provides complementary information since it probes the primary processes initiated by the absorption of a photon and is predominantly sensitive to local effects. Our pump-probe experiments on different systems with 30 fs time resolution show that it is possible to discriminate between different relaxation scenarios and to provide absolute numbers for the local mobility. For thin microcrystalline pentacene films we find that the originally excited Frenkel excitons decay within 70 fs to a non fluorescing species which is still mobile. Its exact nature is currently under investigation. The subsequent decay of the exciton population can be modeled assuming that diffusion driven exciton-exciton annihilation

takes place and a significant concentration of traps exists which can immobilize the excitons. A diffusion constant of $5 \cdot 10^4 \text{ cm}^2/\text{s}$, a trap concentration of $2 \cdot 10^{19} \text{ cm}^{-3}$, and a lifetime of 850 ps for the trapped excitons are obtained.[1] In unordered polymers the large spreading of site energies restricts the exciton diffusion length. To circumvent this problem perylene bisimide dyes are incorporated in a polymer matrix with a high concentration to allow for exciton migration via Förster energy transfer. A fast transfer of 1.5 ps between the dye molecules is derived from the anisotropy decay indicating efficient exciton migration.[2] However, the lifetime of the excitons is limited due to trapping by dimers. In the next step we want to avoid the dimer formation and to achieve diffusion lengths in the order of the layer thickness. To look into the dynamics of one dimensional systems perylene bisimide aggregates are investigated. Here an ultrafast relaxation associated with weak signal oscillations is found pointing to the formation of excimers. On the picosecond time scale no further signal changes are observed indicating that the excimers are immobile and annihilation processes do not occur.

[1] H. Marciniak, M. Fiebig, M. Huth, S. Schiefer, B. Nickel, F. Sel-

maier, and S. Lochbrunner, Phys. Rev. Lett. **99** (2007) 176402.
 [2] M. Schlosser and S. Lochbrunner, J. Phys. Chem. B **110** (2006) 6001.

MO 3.2 Mo 14:30 3G

Three-Pulse-Spectroscopy in neat water and aqueous solution — ●MARTIN K. FISCHER, HRISTO IGLEV, and ALFRED LAUBEREAU — Physik-Department E11, Technische Universität München, 85748 Garching, Germany

The ultrafast generation and solvation of electrons in liquids is studied by pump-repump-probe spectroscopy. The application of a third pulse to excite the precursors of the fully hydrated electron leads to the manipulation of the relaxation process.

The technique was applied to study the dynamics in neat H₂O, 15mMol NaBr and 15mMol NaI aqueous solutions. The measured transients are compared to the corresponding pump-probe data. The observed increase in the yield of the long-lived hydrated electrons leads to a novel information about the generation process.

MO 3.3 Mo 14:45 3G

Ultrafast thermal melting of bulk ice — ●STANISLAV PANDELOV, MARCUS SCHMEISSER, HRISTO IGLEV, and ALFRED LAUBEREAU — Physik-Department E11, Technische Universität München, 85748 Garching, Germany

Melting of ice is the most common structural transition and can provides us information about the microstructure of water. The ice-water phase transition after an ultrafast temperature jump is studied in protonated and isotopically mixed ice using 2-color IR spectroscopy [1, 2]. For energy depositions beyond the limit of superheating of the solid phase (330 ± 10 K) [3] partial melting is observed. The process occurs in two steps: (i) ultrafast thermal bulk melting of the excited ice lattice within 5 ± 2 ps and (ii) secondary melting at the generated phase boundaries with a time constant of 33 ps [3]. The latter process (interfacial melting) is found to consume energy amounts in agreement with the latent heat of melting and is accompanied by an accelerated temperature and pressure decrease of the residual ice component. This results support a thermally-driven melting mechanism starting with homogeneous nucleation in the bulk.

[1] H. Iglev, M. Schmeisser, K. Simeonidis, A. Thaller, A. Laubereau, Nature **439** 183 (2006).

[2] M. Schmeisser, A. Thaller, H. Iglev, A. Laubereau, New J Phys **8** (2006).

[3] M. Schmeisser, H. Iglev, A. Laubereau, J Phys Chem B **111** 11271 (2007).

MO 3.4 Mo 15:00 3G

Direct Femtosecond Observation of Tight and Loose Ion Pairs upon Photoinduced Bimolecular Electron Transfer — ●KATRIN ADAMCZYK¹, OMAR F. MOHAMMED², NATALIE BANERJI², JENS DREYER¹, BERNHARD LANG², ERIK T. J. NIBBERING¹, and ERIC VAUTHEY² — ¹Max Born Institut für Nichtlineare Optik und Kurzzeitspektroskopie, Max Born Strasse 2A, D-12489 Berlin, Germany — ²Department of Physical Chemistry, University of Geneva, 30 Quai Ernest-Ansermet, CH-1211 Geneva 4, Switzerland

Photoinduced bimolecular electron transfer reactions have been subject of intensive chemical dynamics research for many decades [1]. These processes play a key role in many areas of chemistry and biology, among these are photosynthesis, solar energy conversion, ET in proteins and biocatalysis. Generally accepted models suppose that charge separation in polar solvents leads to two geminate ion pairs, namely loose or solvent-separated ion pairs (LIPs) and tight or contact ion pairs (TIPs). We show that monitoring marker modes of the ion products [2] with polarisation-sensitive ultrafast infrared spectroscopy enables a differentiation of the contributions of these distinct ion pairs in the observed kinetics. We find that large exergonic electron transfer reactions predominantly occur in tight donor-acceptor pairs. Tight ion pairs are found to be highly anisotropic, revealing the importance of mutual orientation of the reactants and thus demanding refinement of theoretical models relying on spherical reaction species that solely involve reaction distances. [1] A. Weller, Pure Appl. Chem. **54**, 1885 (1982). [2] O. F. Mohammed et al., J. Phys. Chem. A **110**, 13676 (2006).

MO 3.5 Mo 15:15 3G

Charakterisierung der Femtosekunden Mehrphotonen-Ionisation von N₂ durch rotationsaufgelöste Fluoreszenzspektroskopie — ●ANDREAS WIRSING¹, JÜRGEN PLENGE¹, CHRISTOPHER RASCHPICHLER¹, MICHAEL MEYER² und ECKART RÜHL¹ — ¹Physikalische und Theoretische Chemie, Institut für Chemie und Biochemie, Freie Universität Berlin, Takustr. 3, 14195 Berlin — ²LIXAM, Centre Universitaire Paris-Sud, Batiment 350, F-91405 Orsay Cedex, Frankreich

Die Wechselwirkung von N₂ mit Femtosekunden-Laserpulsen wurde in den letzten Jahren eingehend untersucht. Zur Charakterisierung der dabei auftretenden Ionisationsprozesse werden gewöhnlich die gebildeten Ionen oder Photoelektronen detektiert. Ein komplementärer Ansatz beruht auf der Fluoreszenzspektroskopie, die es im Gegensatz zur Photoelektronenspektroskopie aufgrund der höheren Auflösung ermöglicht, die Rotationsverteilung der elektronisch angeregten Stickstoffionen präzise zu ermitteln. Wir präsentieren rotationsaufgelöste Fluoreszenzspektren von N₂⁺ (B ²Σ_u⁺ → X ²Σ_g⁺ Übergang) nach der Multiphotonen-Ionisation von molekularem Stickstoff mit Femtosekunden-Laserpulsen bei λ=803,4 nm. Aus den Fluoreszenzspektren wird die Rotationsanregung von N₂⁺ (B ²Σ_u⁺) ermittelt. Bei der Ionisation mit einem nahezu transformlimitierten Laserpuls wird eine Anregung der Rotationsniveaus J⁺ = 1 bis J⁺ = 32 des Ions beobachtet. Durch den Einsatz von gechirpten Laserpulsen kann die Rotationsanregung von N₂⁺ (B ²Σ_u⁺) kontrolliert werden. Mögliche Mechanismen der Kontrolle der Rotationsanregung werden diskutiert.

MO 3.6 Mo 15:30 3G

Few photon induced dissociative ionization of N₂ at FLASH — ●YUHAI JIANG¹, LUTZ FOUCAR², ARTEM RUDENKO¹, MORITZ KURKA¹, CLAUDIUS DIETER SCHRÖTER¹, THORSTEN ERGLER¹, KAI UWE KÜHNEL¹, MARKUS SCHÖFFLER², SVEN SCHÖSSLER², TILO HAVERMEIER², MATHIAS SMOLARSKI², KYRA COLE², THORSTEN WEBER², REINHARD DÖRNER², STEFEN DÜSTERER³, ROLF TREUSCH³, PAUL RADCLIFFE³, ELKE PLÖNJES³, MICHAEL GENSCHE³, ROBERT MOSHAMMER¹, and JOACHIM ULLRICH¹ — ¹Max-Planck-Institut für Kernphysik, Saupfercheckweg 1, 69117 Heidelberg — ²Institut für Kernphysik, Universität Frankfurt, D 60486 Frankfurt — ³DESY, Notkestrasse 85, 22607 Hamburg

The Free electron LASer at Hamburg (FLASH) delivers extreme ultraviolet (XUV) radiation at unprecedented intensities with femtosecond pulse durations. In combination with advanced multi-particle detection systems—the Heidelberg reaction microscope—this opens the door for mapping the dissociative multiple-ionization dynamics of molecules at ultrashort time scales. Multiple ionization of N₂ and in particular the fragmentation channels N₂²⁺ → N⁺ + N⁺ and N₂³⁺ → N⁺ + N²⁺ induced by two and three XUV-photon of 44 eV, respectively, have been studied using our coincidence technique. On the basis of the kinetic energy releases of ionic fragments and the known molecular potential curves of dissociative states, it was found that sequential photoabsorption of N₂²⁺ (d³Π_g) → N₂³⁺ occurs at a time of about 20 fs after populating N₂²⁺ by absorption of two photons from the ground state of N₂.

MO 3.7 Mo 15:45 3G

Effect of Size Quantization on Interfacial Electron Transfer Dynamics in TiO₂ Nanoparticles — ●HIRENDRA N. GHOSH — Radiation and Photochemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai-85, India — Max-Born Institute for Nonlinear and Short Pulse Spectroscopy, 12489, Berlin, Germany

Interfacial electron transfer dynamics was carried out in alizarin sensitized TiO₂ nanoparticles with quantum size using femtosecond transient absorption (TA) spectroscopy. The TiO₂ nanoparticles have been synthesized by arrested precipitation method. Electron injection dynamics were found to be multi-exponential with time constants of 100 fs, 17 ps and 50 ps. This observation was explained on the basis discreteness of the conduction band levels due to finite size effect. The back electron transfer (BET) dynamics found to be very slow as compared to the bulk system. The result gives us direct proof of non-adiabatic electron transfer reaction in a strong binding dye like alizarin.

MO 4: Femtosekundenspektroskopie II

Zeit: Montag 16:30–19:00

Raum: 3G

MO 4.1 Mo 16:30 3G

Monitoring Electron Tunneling Dynamics in Molecules with Attosecond Precision — ●STEFANIE GRAEFE and MISHA YU. IVANOV — Steacie Institute for Molecular Sciences, National Research Council Canada, Canada

Recent experiments have demonstrated control of electron localization during strong-field induced ionization and subsequent dissociation of molecular deuterium (D_2) (Kling et al., Science 2006). As the molecular ion D_2^+ created after strong-field ionization vibrates, the returning electron excites the molecular ion into the dissociative σ_u state. Recollision and excitation of the σ_u state occur in the presence of the strong laser field, which creates a coherent superposition of the σ_u and σ_g states. This superposition corresponds to an electron localized on one of the two protons, breaking the symmetry in molecular dissociation.

To observe electronic dynamics, the spectroscopic techniques have to be on the same time-scale as the dynamics to be observed - the attosecond time-scale. Although attosecond pulses are spectrally very broad (several eV), we demonstrate that information about electronic tunneling motion can be extracted by monitoring asymmetries in the time-resolved photoelectron distribution. A theoretical description for calculating time-resolved spectra in the presence of a strong laser field is given. Taking the electronic localization dynamics as an example, it is demonstrated that electron tunneling can be observed by interferences in the photoelectron spectra, based on a mechanism similar to interfering pathways in coherent control (double-slit setup).

MO 4.2 Mo 16:45 3G

Manipulation von Femtosekundenimpulsen im Mittelinfraroten - Schwingungsenergieübertragung in Nitrophenylalanin — ●KARIN HAISER, FLORIAN KOLLER, MARKUS HUBER, NADJA REGNER, WOLFGANG SCHREIER, TOBIAS SCHRADER und WOLFGANG ZINTH — Lehrstuhl für BioMolekulare Optik, Ludwig-Maximilians-Universität München, Oettingenstr. 67, 80538 München

Eine Voraussetzung für die zweidimensionale Infrarotspektroskopie sind spektral schmalbandige und abstimmbare ultrakurze Anregungsimpulse im mittleren Infraroten. Diese Impulse können durch Differenzfrequenzmischung (DFM) von zwei fs-Nahinfrarotimpulsen erzeugt werden. Spektrale Einschränkung erreicht man dadurch, dass den Nahinfrarotimpulsen vor der DFM ein definierter und einstellbarer Chirp aufgeprägt wird. So lassen sich bandbreitebegrenzte schmalbandige Mittelinfrarotimpulse (Dauer ca. 1 ps) erzeugen. Zusätzlich ist eine schnelle, computeransteuerbare Abstimmung der spektralen Lage in einem Bereich von 200 cm^{-1} möglich.

Für ein Anreg-Abtast-Experiment im Mittelinfraroten wurden diese Anregungsimpulse zur Untersuchung der Übertragung von Schwingungsenergie an der Aminosäure Nitrophenylalanin eingesetzt. Dabei wurden verschiedene Schwingungsmoden einzelner Molekülgruppen gezielt angeregt und deren Wechselwirkung untereinander systematisch untersucht. Es konnten Kopplungsmechanismen verschiedener Art beobachtet und teilweise intramolekularen Energierelaxationsprozessen zugeordnet werden.

MO 4.3 Mo 17:00 3G

Molecular sensing with a fibre laser using interferometric nonlinear vibrational spectroscopy — ●BERNHARD VON VACANO, JEAN REHBINDER, TIAGO BUCKUP, and MARCUS MOTZKUS — Physikalische Chemie, Philipps-Universität Marburg, Hans-Meerwein-Strasse, D-35043 Marburg, Germany

Compact fs-fibre lasers promise to make nonlinear spectroscopy available for real-life applications. In a simple scheme, we demonstrate nonlinear vibrational spectroscopy with a single beam of femtosecond pulses from an unamplified fibre laser oscillator. To achieve high spectral resolution and sensitive signal detection with only picojoule pulse energies available, pulse shaping and integrated interferometric detection is employed. The spectroscopic technique used is coherent anti-Stokes Raman scattering (CARS), obtaining well-resolved spectra of molecular vibrations of halomethane samples in the liquid phase, covering $100 - 350\text{ cm}^{-1}$. We explore the implications of phase control for the interferometric detection of weak signals. The presented combination of fiber laser, pulse shaping and CARS microspectroscopy is a first example of simplified schemes for compact and robust nonlinear

spectroscopic detection and sensing, which is demonstrated exemplarily by online monitoring the chemical composition in a microfluidic flow cell.

MO 4.4 Mo 17:15 3G

Femtosecond Dynamics of Phenylcarbenes — ●BASTIAN NOLLER¹, INGO FISCHER¹, LIONEL POISSON², and JEAN-MICHEL MESTDAGH² — ¹Institut für Physikalische Chemie, Universität Würzburg, Deutschland — ²Laboratoire Francis Perrin, CEA Saclay, France

Carbenes play an important role in combustion chemistry and interstellar space and have gained considerable interest in synthesis over the last years. The electronic states of carbenes often have very small energy gaps between each other and are of considerable interest as a "benchmark" for improving quantum mechanical methods. The photophysics of carbenes is not well investigated due to the experimental challenge. The dynamics of several phenylcarbenes (*Ph-C-R*), with a variety of substituents (i.e. $R=CH_3, CF_3, Cl$), were investigated by femtosecond time-resolved pump probe spectroscopy in a free jet. REMPI spectra were recorded with a nanosecond laser setup. The carbenes were produced by jet flash pyrolysis of diazirines. Time-of-flight mass spectrometry, photoion- and photoelectron imaging were employed as detection methods in the femtosecond time-resolved experiments. The excited state dynamics depended on the substituents (*R*) and will be compared to models based on qualitative excited state calculations. Preliminary results indicate that conical intersections along the rotation coordinate of the group *R* against the phenyl ring and/or along the coordinate of a 1,2-H-shift in the excited state play an important roles for state deactivation.

MO 4.5 Mo 17:30 3G

Femtosecond Dynamics of Electron Transfer in a Neutral Organic Mixed-Valence Compound — ●MARKUS MARGRAF¹, JULIANE KÖHLER¹, RAMAN MAKSIMENKA^{1,2}, ALEXANDER HECKMANN¹, CHRISTOPH LAMBERT¹, and INGO FISCHER¹ — ¹University of Würzburg, Department of Chemistry, 97074 Würzburg — ²Laboratoire Francis Perrin, CEA Saclay, F-91191 Gif-sur-Yvette Cedex

A neutral organic mixed valence compound was studied by femtosecond time-resolved transient absorption spectroscopy with the aim to gain insight into its charge-transfer dynamics upon optical excitation. The back electron transfer was investigated in five different solvents: n-hexane, toluene, dibutyl ether, methyl-tert-butyl ether (MTBE) and benzonitrile. In the pump step, the molecule was excited at 760 nm and 850 nm into the intervalence charge-transfer band. The resulting transients can be described by two time-constants. We assign one time-constant to the rearrangement of solvent molecules in the charge transfer state and the second time-constant to back-electron transfer to the electronic ground state. On the one hand we investigated the influence of the solvent polarity on the rate of back electron transfer, on the other hand the dependence on orientation of polarisation between pump- and probepulse. Back electron transfer rates range from $1.5 \cdot 10^{12}\text{ s}^{-1}$ in benzonitrile through $8 \cdot 10^{11}\text{ s}^{-1}$ in MTBE, around $1.6 \cdot 10^{11}\text{ s}^{-1}$ in dibutylether and toluene and to $3.8 \cdot 10^9\text{ s}^{-1}$ in n-hexane.

MO 4.6 Mo 17:45 3G

Determination of electronic transition dipole moment orientations by polarization re-solved femtosecond VIS-pump / IR-probe spectroscopy — MARTIN LINKE, MORITZ THEISEN, ALEXANDRA LAUER, HENK FIDDER, and ●KARSTEN HEYNE — Freie Universität Berlin, Fachbereich Physik, Arnimallee 14, 14195 Berlin, Germany

Excitation of an isotropic ensemble of molecules with linear polarized light pulses leads to an anisotropic distribution of excited molecules (photoselection). During anisotropy decay conformational changes and the orientation of transition dipole moments can be identified by femtosecond polarization resolved pump-probe experiments. We determined the orientations of electronic and infrared transition dipole moments of Coumarin 314 and of Chlorophyll a molecules in solution.

The orientation of the electronic transition dipole moment of the Qy band within the molecular structure of Chlorophyll a is the basis

for simulating many properties of photosynthetic systems. Determinations thus far of the electronic transition dipole moment orientations of Chlorophyll a were made on oriented samples with steady state spectroscopy, and with steady state anisotropy experiments. These experiments yielded angles for the orientation of the Qy electronic transition dipole moment with respect to the x-axis varying from 70° to 90°. Using polarization resolved VIS pump / IR-probe experiments we reinvestigated this issue.

MO 4.7 Mo 18:00 3G

Ultrafast Singlet versus Triplet Dynamics in Thin Pentacene Films — ●HENNING MARCINIAK¹, STEFAN LOCHBRUNNER¹, and BERT NICKEL² — ¹Institut für Physik, Universität Rostock — ²Fakultät für Physik und CeNS, LMU München

Thin pentacene films are frequently applied as active layers in prototypical organic electronic devices. Their electronic structure and dynamics determine to a large extent the device behavior. We investigate with femtosecond absorption spectroscopy microcrystalline pentacene films with a thickness of roughly 30 monolayers. The transient spectra show that optically excited singlet excitons decay within 70 fs to a non fluorescing species [1]. The fission of a singlet exciton into two triplet excitons is discussed as potential relaxation path. The process was observed in crystalline tetracene and the time scale is feasible since the total spin is conserved. By tilting the pentacene layers relative to the incident laser beams it is possible to probe singlets and triplets or exclusively singlets since the transition dipole of the lowest triplet-triplet absorption band is orientated along the long axis of the upstanding molecules. A transient absorption band at 525 nm can thereby be identified as triplet absorption. However, it rises with a time constant of about 0.9 ps instead of 70 fs and it is more than a factor of 10 weaker than expected. We conclude that triplet formation is a secondary step and only a small fraction of excitons experiences fission into triplets. The majority transforms probably to excimer excitons.

[1] H. Marciniak, M. Fiebig, M. Huth, S. Schiefer, B. Nickel, F. Selmaier, and S. Lochbrunner, Phys. Rev. Lett. **99** (2007), 176402.

MO 4.8 Mo 18:15 3G

Heterogeneous Electron Transfer Dynamics in Systematically Varied Perylene/TiO2 Systems — ●ANTJE NEUBAUER, JODI SZARKO, ANDREAS BARTELT, RAINER EICHBERGER, OLAF LETTAU, and CARLO FASTING — Hahn-Meitner-Institut, Berlin

We present fs-transient absorption measurements of perylene dyes attached to TiO2 colloidal films in ultrahigh vacuum and compare the photoinduced electron injection and recombination dynamics.

New perylene derivatives with a systematic structural change were synthesized and chemically bound to nano-structured colloidal anatase films via a carboxylic anchor group. Extending the distance between the aromatic rings of the perylene and the carboxylic anchor group starting with one double bond and going up to five double bonds also changed the photophysical properties of the dyes.

Prior to the fs-transient absorption experiments, the electronic states of the dyes in solution and bound to the TiO2 surface were studied with steady-state absorption and fluorescence spectroscopy. In all these experiments, a systematic red shift of ground, cationic, and excited state

absorption bands were observed with increasing chain length.

Electron injection rates were below 30 fs, with the exception of an additional longer component in the range of 120 fs for the perylene dye with the longest chain. At the same time, the recombination process slowed down significantly with increasing chain lengths. The data suggest strong electronic coupling in the case of electron injection and weaker coupling for electron recombination.

MO 4.9 Mo 18:30 3G

Rotational diffusion measured by optical transient anisotropy — ●OLIVER SCHALK and ANDREAS-NEIL UNTERREINER — Universität Karlsruhe (TH), Lehrstuhl für Molekulare Physikalische Chemie, 76128 Karlsruhe

Rotational diffusion in real time can be observed by transient anisotropy, which is often interpreted in terms of correlation functions. However, anisotropy is sensitive to the transition dipole moment (i.e., only 2 dimensions are to be considered) which leads to a modified decay mechanism. To consider anisotropy explicitly, a new ansatz is shown where rotational diffusion is described by a step model that is able to interpolate between free rotation and media with high viscosities. For collision-free reorientation, a different initial decay and long-time behavior is obtained and compared to models based on correlation functions — however, the new ansatz describes the experiments more satisfactorily. The behavior of collisional anisotropy decay has been modeled by means of Monte-Carlo simulations allowing for a variation of angular correlation and energy transfer. As shown, this approach is easily extendable to multiphoton processes.

MO 4.10 Mo 18:45 3G

Ultrafast Electronic and Vibrational Spectroscopy of LOV1C57S Mutant — ●ALEXANDER WEIGEL and LUIS PEREZ LUSTRES — Institute for Chemistry, Brook-Taylor-Str. 2, 12489 Berlin

The photoactivation of Phot proteins involves two LOV-domains binding flavin mononucleotide as a chromophore. We utilized femtosecond transient absorption spectroscopy to identify the earliest events succeeding the excitation of the C57S mutant of *Chlamydomonas reinhardtii* LOV1 domain. In accordance with literature the excited S₁ state was found to decay with a lifetime of ~2 ns accompanied by a rise of the triplet state spectrum. Several additional features were observed on the shorter timescale. Directly after excitation spectral hole burning reveals the vibrational structure of the transient spectra. Rearrangement of the active site and intramolecular vibrational redistribution lead to a subsequent broadening with time constants of 100 fs and 1 ps. The time traces show pronounced oscillatory behaviour, at least six frequencies between 41 cm⁻¹ and 420 cm⁻¹ could be extracted. Two types of oscillations may be distinguished. One part bears a varying phase over the spectral bands and is clearly attributed to vibrational wavepacket motion. The rest exhibits constant phase behaviour and could stem from vibronic coupling to a nπ* state in the vicinity of S₁. In accordance with this model an evolution with a time constant of 190 ps and a similar spectral distribution is observed. It is intended to use femtosecond stimulated resonance Raman spectroscopy to further clarify the origin of the oscillations and gain additional insight into structural rearrangements. Preliminary results are presented.

MO 5: Photochemie I

Zeit: Dienstag 8:30–10:30

Raum: 3F

Hauptvortrag

MO 5.1 Di 8:30 3F

The Photochemistry of N-Oxides - A White Spot in Femtosecond Spectroscopy — THORBEN CORDES, NADJA REGNER, ELINA BORYSOVA, BJÖRN HEINZ, and ●PETER GILCH — Lehrstuhl für BioMolekulare Optik, Fakultät für Physik, LMU München, Oettingenstr. 67, D-80538 München

Organic compounds containing an imino N-oxide function (=N⁺-O⁻) have been known to be photo-reactive for a more than a century. This photo-reactivity has been observed e.g. for azoxy (N=N⁺-O⁻) compounds, nitrene (C=N⁺-O⁻) derivatives, and heterocyclic N-oxides and proves to be very general. Numerous examples have been compiled [1,2]. These photo-reactions pave the way to products difficult to access otherwise. But although photo-reactivity is a general feature of N-oxides there are various possible outcomes of these reactions. For instance, upon illumination the N-oxide of isoquinoline transforms into

a lactam, whereas its cyano substituted derivative yields an oxazepine [3]. The difference in product formation has been associated with the intermediacy of a radical pair in the first and an oxaziridine in the second case. In some cases such oxaziridines - three membered rings containing the N and O atoms of the former N-oxide - have been isolated [1]. Yet, their intermediacy in most reactions has until now only been postulated. In fact, the whole photochemistry of N-oxides has not been paid much attention by femtosecond spectroscopists.

We have started a research program trying to fill this "white spot". As a starting point, the complex photo-rearrangement of a heterocyclic N-oxide, 2-benzoyl-3-phenylquinoxaline-1,4-dioxide, in solution phase has been addressed by means of femtosecond spectroscopy. This N-oxide transforms into an imidazolone with a quantum yield of 10 % [4]. Transient absorption spectroscopy in the femto- to microsecond range reveals slightly solvent dependent kinetic compounds with time

constants (in ethanol) of 1 ps, 10 ps, 200 ps, and 200 ns. The slowest component represents the final product formation. Femtosecond fluorescence spectroscopy associates the 1 ps and 10 ps time constants with excited state relaxation and depletion processes, respectively. For the 10 ps, 200 ps, and 200 ns processes indications for a kinetic branching involving ground state recovery and population of intermediates are observed. The measurements are complemented by femtosecond IR experiments which aim at a structural assignment of the intermediates. Based on these data a kinetic model for the photo-reaction will be derived and prospects of our research on N-oxides are given.

- [1] A. Albini, M. Alpegiani, Chem. Rev. 84 (1984) 43
 [2] G.G. Spence, E.C. Taylor, O. Buchardt, Chem. Rev. 70 (1970) 231
 [3] N. Hata, Bull. Chem. Soc. Jpn. 58 (1985) 1088
 [4] N.A. Masoud, J. Olmsted, III, J. Phys. Chem. 79 (1975) 2214

MO 5.2 Di 9:00 3F

Solvent effects in the excited state reaction dynamics of molecular switches — •FLORIAN J. LEDERER¹, STEPHAN MALKMUS¹, THOMAS BRUST¹, SIMONE DRAXLER¹, JESSICA A. DIGIROLAMO², WATSON J. LEES², WOLFGANG ZINTH¹, and MARKUS BRAUN¹ — ¹Ludwig-Maximilians-Universität München, Lehrstuhl für BioMolekulare Optik, — ²Department of Chemistry and Biochemistry, Florida International University

Indolyfulgides exhibit a photochemical ring-opening/ring-closure reaction on the picosecond timescale. The different isomers are thermally stable and have strongly separated absorption bands, which facilitate their use as optical memory elements.

We performed femtosecond-spectroscopy to study the ring-opening reaction of a fluorinated indolyfulgid in different solvents. The temperature-dependent time constants and quantum yields of the reaction are explained by an activated behaviour: the ring-opening evolves over a barrier.

This barrier is influenced by the surroundings of the molecule. Onsager and Kirkwood gave an approximation for the energy displacement of a single molecule due to the change of the dielectric properties of the solvent. In combination with a Marcus-like model, this approximation can be used to describe the influence of the solvent on the photochemical reaction.

MO 5.3 Di 9:15 3F

Chemische Kontrolle der photoinduzierten Z/E Isomerisierung von Hemithioindigoverbindungen — •THORBEN CORDES¹, TORSTEN SCHADENDORF², KAROLA RÜCK-BRAUN² und WOLFGANG ZINTH¹ — ¹LMU München, Lehrstuhl für BioMolekulare Optik, Oettingenstraße 67, 80538 München — ²TU-Berlin, Institut für Chemie, Straße des 17. Juni 135, 10623 Berlin

Die photoinduzierte Z/E-Isomerisierung von Hemithioindigoverbindungen läuft auf einer Pikosekundenzeitskala ab [1]. In diesem Beitrag wird der Einfluss von Substituenten (Methoxy, Brom, Chlor, Cyano) auf den kinetischen Ablauf der Reaktion untersucht. Dabei zeigen sich für das asymmetrische HTI-Molekül sehr deutliche Änderungen der Reaktionsgeschwindigkeit. Diese hängen sowohl von den elektronischen Eigenschaften sowie der Position des jeweiligen Substituenten ab: hierbei zeigt sich ein inverser Einfluss der Substituenten für ihre Stilben- und Thioindigo-Substitution. Diese Ergebnisse werden auf molekularer Ebene gedeutet und in ein Reaktionsmodell eingebettet. [1] T. Cordes et al. ChemPhysChem 8 (2007) 1713-1721

MO 5.4 Di 9:30 3F

Photochrome Fulgide als molekulare Bits – Optischer Speicher mit 250 GHz Taktrate — •SIMONE DRAXLER¹, STEPHAN MALKMUS¹, FLORIAN O. KOLLER¹, THOMAS BRUST¹, JESSICA A. DIGIROLAMO², WATSON J. LEES², WOLFGANG ZINTH¹ und MARKUS BRAUN¹ — ¹Lehrstuhl für BioMolekulare Optik, Fakultät für Physik, Ludwig-Maximilians-Universität München — ²Department of Chemistry and Biochemistry, Florida International University Miami, USA
 Das Konzept eines ultraschnellen Schreib-Lese-Lösch-Lese-Zyklus eines Systems basierend auf einem photochromen Indolyfulgid wird vorgestellt [1]. Zur binären Kodierung von Information wird hierbei die Struktur des verwendeten Farbstoffs auf molekularer Ebene zwischen zwei thermisch stabilen Zuständen mit Lichts geeigneter Wellenlänge

hin- und zurückgeschaltet. Zerstörungsfreies Auslesen der Bitzustände mittels infrarotem Licht vervollständigt den Entwurf eines optischen Speichers. Für den ultraschnellen Betrieb werden Femtosekunden-Lichtimpulse verwendet. Hier wird demonstriert, dass aufeinanderfolgende Schreib- und Löschprozesse mit weniger als 4 ps Abstand immer noch ein definiertes Auslesen der Bitzustände ermöglichen. Die kurze Zeitverzögerung zwischen den Schreib-, Lösch- und Lesevorgängen zeigt, dass ein auf Indolyfulgiden basierendes optisches Speichersystem bei Taktraten von über 250 GHz betrieben werden kann.

- [1] Malkmus et al. Adv. Funct. Mater. DOI: 10.1002/adfm.200700553

MO 5.5 Di 9:45 3F

Einfluss thermischer und optischer Überschussenergie auf die ultraschnelle Photochemie von Indolyfulgiden — •THOMAS BRUST, SIMONE DRAXLER, STEPHAN MALKMUS, WOLFGANG ZINTH und MARKUS BRAUN — Lehrstuhl für BioMolekulare Optik, Fakultät für Physik, Ludwig-Maximilians-Universität München

Fulgide sind photochrome molekulare Schalter, die durch Absorption von Licht reversibel ihre Struktur ändern können. Diese E/Z-Isomerisations-, Ringschluss- oder Ringöffnungsreaktionen sind ultraschnell [1]. Insbesondere die Klasse der Indolyfulgide zeichnet sich dabei durch thermische und chemische Stabilität ihrer Isomere aus.

Wir untersuchen die Dynamik und die Reaktionsausbeute der Ringöffnung von Indolyfulgiden und verwandten Indolyfulgimiden mittels Femtosekunden- und Dauerstrichspektroskopie. Die transienten Absorptionsmessungen zeigen, dass die Reaktionszeiten im Bereich einiger Pikosekunden liegen. In unpolaren Lösungsmitteln ist die Reaktionsgeschwindigkeit schneller und die Quantenausbeute höher als in polarer Umgebung. Ebenso zeigt sich neben einer Temperaturabhängigkeit auch eine Abhängigkeit von der Anregungswellenlänge. Diese stellt eine Ausnahme der Kasha-Vavilov-Regel dar und wird hier in einem Modell beschrieben.

- [1] S. Malkmus et al., Chem. Phys. Lett. 417 (2006) 266-271

MO 5.6 Di 10:00 3F

Untersuchung der photochemischen und thermischen Reaktionen von Anthracen-9,10-endoperoxid — •ALEXANDRA LAUER, HENK FIDDER und KARSTEN HEYNE — Freie Universität Berlin

Anthracen-9,10-endoperoxid kann in Abhängigkeit von der Anregungswellenlänge unterschiedliche photoinduzierte Reaktionen eingehen. Die dabei entstehenden Reaktionsprodukte wurden mit Hilfe von Absorptions-, Emissions- und Emissions-Anregungs-Spektren nach Lichtanregung unter verschiedenen Bedingungen untersucht; dabei wurden insbesondere die Anregungswellenlänge und die Proben temperatur systematisch variiert. Die zeitliche Veränderung metastabiler Primärprodukte wurde verfolgt und die Ergebnisse im Hinblick auf Reaktionsmechanismen analysiert. Dabei wurden auch die Produkte der thermisch induzierten Reaktion zum Vergleich herangezogen. Erste Ergebnisse dieser Untersuchungen sollen hier kurz vorgestellt werden.

MO 5.7 Di 10:15 3F

Untersuchung des ersten Anregungszustandes bei der 2-Photonenanregung von gelöstem und amorphem Melanin mit linearen und nichtlinearen spektroskopischen Methoden — •GUNTER SEEWALD¹, DIETER LEUPOLD¹, MATTHIAS SCHOLZ¹, CHRISTIAN SPITZ² und RALF MENZEL² — ¹LTB GmbH, 12489 Berlin, Rudower Chaussee 29 — ²Institut für Physik, Photonik, Universität Potsdam

Melanin ist ein Makromolekül welches zu den organisch erzeugten "black materials" gehört und somit als hocheffizienter Photonen-Phononen-Wandler wirkt. Es kommt in allen Lebewesen vor und dient u.a. als Lichtschutz, Schalldämmung, Stoffspeicher und Radikalfänger. Trotz jahrzehntelanger Forschung sind die Struktur und der Energietransport innerhalb des Melanins aufgrund seiner Komplexität nur ansatzweise geklärt. Im Gegensatz zu konventionellen Fluorophoren besitzt Melanin eine spektral kontinuierliche Absorption, eine sehr schwache Fluoreszenz bei 1-Photonen-Anregung sowie die Möglichkeit zu einer schrittweisen 2-Photonen-Anregung. Es werden mögliche Modelle für den intra- und innermolekularen Energietransport diskutiert - ausgehend vom ersten elektronischen Anregungszustand, der mit linearen und nichtlinearen spektroskopischen Methoden untersucht wurde.

MO 6: Photochemie II

Zeit: Dienstag 11:00–13:00

Raum: 3F

MO 6.1 Di 11:00 3F

Zweiphotonenangeregte Fluoreszenz an Rhodaminen — ●ANDREAS GARZ, CHRISTIAN SPITZ und RALF MENZEL — Universität Potsdam, Germany

Die simultane Zwei-Photonen-Absorption, bei der jedes Photon die Hälfte der Übergangsenergie aufbringt, hat eine quadratische Intensitätsabhängigkeit. Dies wird anhand der Fluoreszenzintensität als Funktion der Anregungsintensität mit fs Pulsen und Anregungsintensitäten bis 10^{12} W/cm² demonstriert. Vorgestellt werden intensitätsabhängige Messungen der Fluoreszenzintensität verschiedener Rhodamine (123, 6G, B). Dabei ist zu beobachten, dass ab einer konzentrationsabhängigen Schwellintensität die Fluoreszenz mit zunehmender Anregungsintensität wieder abnimmt, was auf die energetisch passende Excited State Absorption (ESA) von Rhodamin zurückgeführt wird. Weiterhin wird beobachtet, dass die Fluoreszenz, nachdem sie um zwei Größenordnungen zurückgegangen ist, für noch höhere Anregungsintensitäten wieder mit der Anregung ansteigt. Der dabei beobachtete Anstieg ist uneinheitlich für die untersuchten Moleküle und wird auf der Grundlage von Ratengleichungen diskutiert.

MO 6.2 Di 11:15 3F

Frenckel Exzitonen auf molekularen Aggregaten zwischen 10 und 330 K — ●CHRISTIAN SPITZ, ANTONIO SAGHATI und RALF MENZEL — Universität Potsdam, Deutschland

Auf ausgedehnten Farbstoffaggregaten können optische Anregungszustände aufgrund der Dipol-Dipol Wechselwirkung delokalisieren. Auf J-Aggregaten erreichen diese Anregungszustände als so genannte Frenckel Exzitonen einen im Vergleich zum Einzelmolekül um Größenordnungen erhöhten Wirkungsquerschnitt. Die energetische und räumliche Propagation dieser Exzitonen hängt stark von dem Ordnungsgrad und somit der Temperatur der Aggregate ab. Obwohl die J-Aggregate bereits seit 1936 bekannt sind, wirft die Temperaturabhängigkeit der Exzitonenpropagation noch Rätsel auf und wird durch zwei theoretische Ansätze unterschiedlich beschrieben. In diesem Beitrag werden erstmals Messungen an einer Aggregatpräparation vorgestellt, die eine Variation der Temperatur zwischen 10 K und 330 K ohne Phasenübergang erlaubt. Anhand der experimentellen Ergebnisse werden die beiden Theorien verglichen.

MO 6.3 Di 11:30 3F

Zeitaufgelöste ns-Spektroskopie an heterozyklischen N-Oxiden — ●NADJA REGNER, THORBEN CORDES und PETER GILCH — LMU München, Lehrstuhl für BioMolekulare Optik, Oettingenstraße 67, 80538 München

Photoreaktionen von heterozyklischen N-Oxiden sind nützliche synthetische Werkzeuge zur Erzeugung von anderweitig schwer zugänglichen Substanzen. Eine große Anzahl von verschiedenen N-Oxiden zeigt photoinduzierte Umlagerungsreaktionen. Die Umwandlung eines bestimmten N-Oxids (2-Benzoyl-3-phenyl-quinoxaline-1,4-Dioxid) in ein Imidazolone vollzieht sich mit einer Quantenausbeute von 10% und wurde mit verschiedenen spektroskopischen Techniken untersucht [1,2].

Mit Hilfe von transienter Absorptionsspektroskopie konnte ein Reaktionsmodell für unmittelbar nach der Photoanregung stattfindende Prozesse aufgestellt werden [2]. In dem maximalen Zeitfenster von 3.5 ns, welches bisher bei diesen Experimenten zur Verfügung stand, zeigte sich noch keine Produktbildung. Dieser Beitrag stellt nun zeitaufgelöste Messungen im Nanosekunden- und Mikrosekundenbereich vor, die es ermöglichen, die Photoumlagerung zum Produkt auf einer Zeitskala von 300 ns zu beobachten. Dank der neuen Ergebnisse kann der Reaktionsverlauf in einem Zeitbereich von 100 fs bis 1 μ s verfolgt werden. Das bestehende Modell [2] kann nun um die Produktbildung erweitert werden.

[1] N. A. Masoud and J. Olmsted III, J. Phys. Chem. 21 (1975) 2214-2220 [2] T. Cordes, N. Regner, F. Michalik, P. Gilch, TRVS XIII Proceedings (2007) 151-153

MO 6.4 Di 11:45 3F

Molecular Ion Photodissociation at FLASH — ●BRANDON JORDON-THADEN¹, HENRIK B. PEDERSEN², SIMON M. ALTEVOGT¹, ODED HEBER³, LUTZ LAMMICH², MICHAEL RAPPAPORT³, DIRK SCHWALM¹, DANIEL ZAJFMAN³, JOACHIM ULLRICH¹, ANDREAS WOLF¹, MARKO FÖRSTEL⁴, TORALF LISCHKE⁴, UWE HERGENHAHN⁴, ROLF

TREUSCH⁵, NATALIA GUERASSIMOVA⁵, and MICHAEL MARTINS⁶ — ¹Max-Planck-Institut für Kernphysik, 69117 Heidelberg, Germany — ²Department of Physics and Astronomy, University of Aarhus, Aarhus, 8000, Denmark — ³Department of Particle Physics, Weizman Institute of Science, Rehovot, 76100, Israel — ⁴Max-Planck-Institut für Plasmaphysik, EURATOM Association, 85748 Garching, Germany — ⁵HASYLAB, DESY, 22607 Hamburg, Germany — ⁶Institut für Experimentalphysik, Universität Hamburg, 22671 Hamburg, Germany

Using the novel intense vacuum-ultraviolet (VUV) photon source at the Free-electron LASer facility in Hamburg (FLASH), excited state photodissociation of the benchmark system HeH⁺ has recently been performed in a crossed beams setup (TIFF). A program on photofragmentation of water-based ions has been initiated beginning with H₂O⁺ and H₃O⁺ and progressing towards weakly bound water clusters (H₂O)_NLi⁺. FLASH in combination with the fast beam momentum fragment imaging system and a photoelectron spectrometer would offer insights on e.g. Electron Transfer Mediated Decay (ETMD) processes. We will describe novel experimental developments at TIFF and review efforts to produce intense beams of weakly bound water cluster ions.

MO 6.5 Di 12:00 3F

Coherently Controlled Release of Drugs in the Ophthalmology — ●TIAGO BUCKUP, JENS MÖHRING, VOLKER SETTELS, JENS TRÄGER, HEE-CHEOL KIM, NORBERT HAMPP, and MARCUS MOTZKUS — Physikalische Chemie, Philipps Universität Marburg, D-35043 Marburg, Germany

The release of drugs using photochemical cleavable link molecules is an important method in the modern treatment of eyes diseases. The decisive step in this application is the controlled cleavage of the coumarin dimer link system using two-photon excitation. This way, the photochemical release can be exclusively controlled with laser irradiation when required and not triggered with day light. In this work, we investigate in open- and closed-loop control schemes the optimal pulse solution to achieve an efficient two-photon induced cleavage. The optimization of the dicoumarin cleavage reaction was performed using the shaped emission of a non-collinear optical parametric amplifier at 532nm in a novel accumulation absorption setup based on a capillary as probe holder. In this setup, a defined sample volume is irradiated for a short period with a tailored pulse and the reaction conversion efficiency is probed at 310nm, the absorption maximum of the coumarin monomer. Closed-loop optimizations targeting the maximization of the reaction yield and the minimization of a two-photon dependent signal shows that a Fourier-limited pulse (18fs) is not the best suitable pulse to steer the reaction. Principal component analysis and open-loop scans with defined parameterizations are used to investigate the optimal solutions.

MO 6.6 Di 12:15 3F

Phasen-Kontrolle der molekularen Fragmentierung von Xylol mit einem Paar von fs-Laserpulsen — ●HANS GEORG BREUNIG, GUNTER URBASCH und KARL-MICHAEL WEITZEL — Fachbereich Chemie, Universität Marburg, Marburg, Germany

Verschiedene Aspekte der Phasenkontrolle molekularer Fragmentierungsprozesse haben in den vergangenen Jahren große Aufmerksamkeit auf sich gezogen. In diesem Beitrag beschreiben wir einen neuen Zugang zur Phasen-Kontrolle basierend auf einem interferometrischen Experiment mit einem Paar von fs-Laserpulsen. Hier entspricht der zeitliche Pulsabstand direkt einer Phasenverschiebung der oszillierenden elektrischen Felder der beiden Teilpulse. Als Beispiel untersuchen wir die dissoziative Ionisation von Xylol. Für den Bereich des zeitlichen Überlapps der beiden Teilpulse folgen alle beobachteten Ionensignale der Intensität des interferierenden Pulspaars, die wiederum mit der Trägerfrequenz des Laserpulses oszilliert (800 nm, 2.7 fs Periode). Für Verzögerungszeiten etwas grösser als die mittlere Pulsdauer beobachten wir eine Phasenverschiebung zwischen verschiedenen Fragment-Ionen, z.B. ausgeprägt zwischen den Fragment-Ionen C⁺ und CH₃⁺. Diese Phasenverschiebung wird als klare Manifestierung einer optischen phasenabhängigen elektronischen Anregung, die unmittelbar auf eine Kerndynamik (molekulare Fragmentierung) abgebildet wird, interpretiert. Dies bedeutet, dass wir über eine Kontrolle der Elektronen die chemischen Prozesse kontrollieren. Es ergeben sich interessante Schlussfolgerungen für die Relevanz der Born-Oppenheimer-Näherung.

MO 6.7 Di 12:30 3F

Inducing chemical reactions in doped quantum solids with vibrons — ●DAVID ANDERSON¹, FALK KÖNIGSMANN², NINA OWSCHMIKOW², and NIKOLAUS SCHWENTNER² — ¹Department of Chemistry, University of Wyoming, Laramie, WY 82071, USA — ²Freie Universität Berlin, Institut für Experimentalphysik, Arnimallee 14, D-14195 Berlin

Solid parahydrogen quantum crystals doped with reactive species are potentially well suited for quantum control experiments. At liquid helium temperatures the entire solute-solvent condensed phase system resides in a nearly pure ground vibronic state and the internal vibrational coordinate of H₂ can be exploited to selectively deliver energy to the reagents to trigger reaction. In situ 355 nm photodissociation of Cl₂ and Br₂ precursor molecules is an effective way to produce Cl and Br atom doped solid parahydrogen. Infrared-active vibrons (intramolecular H₂ stretching modes) of Cl-atom doped solid parahydrogen have been shown [1] to trigger the reaction Cl+H₂ → HCl+H. Systematic studies in solid H₂, HD and D₂ show widely varying reaction rates, a signature that the vibron induced mechanism involves H-atom tunneling. Currently we are investigating if ultrafast pulses can be utilized to excite coherent phonon motions [2] within solid parahydrogen with the aim of developing coherent control schemes for halogen molecules and atoms trapped in solid parahydrogen. [1] P. L. Raston and D. T. Anderson, *Phys. Chem. Chem. Phys.* 8, 3124 (2006). [2] M. Gühr, M. Bargheer, M. Fushitani, T. Kiljunen, and N. Schwentner, *Phys. Chem.*

Chem. Phys. 9, 779 (2007).

MO 6.8 Di 12:45 3F

Beobachtung und Kontrolle laserinduzierter Reaktionen an Einkristalloberflächen — ●PATRICK NUERNBERGER¹, DANIEL WOLPERT¹, HORST WEISS² und GUSTAV GERBER¹ — ¹Physikalisches Institut, Universität Würzburg, Am Hubland, 97074 Würzburg — ²BASF AG, Polymer Research Division, 67056 Ludwigshafen

Wir präsentieren Experimente zur induzierten Bindungsknüpfung und Molekülbildung mit Femtosekunden-Laserimpulsen. Dies wird exemplarisch für die Reaktion von Wasserstoff (H₂) mit Kohlenmonoxid (CO) auf einer Pd(100)-Oberfläche demonstriert. Experimente mit anderen Substanzen werden ebenfalls diskutiert.

Im entwickelten experimentellen Konzept wird ein Gasmisch, bestehend aus kleinen Eduktmolekülen, auf eine Einkristalloberfläche unter Hochvakuum geströmt und mit intensiven Femtosekunden-Laserimpulsen bestrahlt. Die erzeugten Ionen werden mit einem Flugzeitmassenspektrometer analysiert, wobei sich Ionen von Produktmolekülen nachweisen lassen, die in der Wechselwirkung der Gase mit der Oberfläche und dem Laser entstehen.

Durch Anwendung eines rückkopplungsgesteuerten evolutionären Algorithmus werden zudem speziell an die Reaktion angepasste Laserimpulse ermittelt. Diese ermöglichen es, die Verhältnisse der Produktionen selektiv zu verändern und somit die Bildung bestimmter Moleküle zu optimieren.

MO 7: Quantenkontrolle

Zeit: Dienstag 14:00–16:00

Raum: 3F

MO 7.1 Di 14:00 3F

Coherent control of excited state dynamics in a Pump Degenerate-Four-Wave-Mixing (Pump-DFWM) experiment — ●JÜRGEN HAUER¹, TIAGO BUCKUP¹, JUDITH VOLL², REGINA VIVIE-RIEDLE², and MARCUS MOTZKUS¹ — ¹Physikalische Chemie, Philipps-Universität Marburg, D-35043 Marburg, Germany — ²Department Chemie, Ludwig-Maximilians-Universität München, D-81377 München, Germany

Coherent control is generally known as a method for aim directed manipulation of the interaction between light and matter. In literature, there are numerous examples where coherent control favours certain target quantum states while suppressing unwanted ones. We further the concept of modulated light-matter interaction to a novel kind of spectroscopy termed Quantum Control Spectroscopy (QCS), where molecular features hidden from Fourier-limited excitation are brought to light by phase-modulated pulses. As an example, we investigate β -carotene with Pump-Degenerate Four Wave Mixing (Pump-DFWM). Scanning the relative phase between the sub-pulses of a pulse sequence reveals a low-frequency coupling mode near 200 cm⁻¹ between the first two excited states S₂ and S₁. Besides this novel feature, we also show that differently spaced multipulses affect the ultrafast lifetime of the initially populated S₂-state. We substantiate our findings by an in-depth theoretical analysis based on wavepacket dynamics, exhibiting a quantitative agreement between theory and experiment. In a final set of investigations, we explore the degree to which vibrational cooling can be coherently controlled or averted by phase modulation.

MO 7.2 Di 14:15 3F

Femtosecond Pump-DFWM Spectroscopy for the Investigation of the Dynamics of Higher Excited States — ●ABRAHAM SCARIA, VINU NAMBOODIRI, JAKOW KONRADI, JÖRG LIEBERS, ULRICH KLEINEKATHÖFER, and ARNULF MATERNY — Jacobs University Bremen, Germany

Time resolved nonlinear four-wave mixing (FWM) techniques have become valuable tools to investigate dynamic properties of molecules. However until now, FWM techniques were only applied to investigate the dynamics of the ground state or the low lying excited states. Here, we demonstrate that by using an initial pump pulse followed by a time-resolved DFWM process, dynamics of higher lying excited states can be accessed and probed. Since iodine is well characterized by different spectroscopical techniques, it presents itself as an ideal model system for this study. In our experiments [1], the initial pump in the visible was chosen to be resonant with the ground to B state absorption of iodine while the DFWM beams were resonant with the B to ion-

pair state transition. Applying different pulse sequences in the pump-DFWM scheme, wave packets on different potential energy surfaces could be prepared and their dynamics analyzed. In our contribution, we will present experimental results, where the dynamics of ion-pair states belonging to two different tiers were monitored and compared to quantum dynamical simulations. The simulations are detailed in a separate contribution.

[1] A. Scaria, V. Namboodiri, J. Konradi, and A. Materny, *J. Chem. Phys.* **127**, 144305 (2007)

MO 7.3 Di 14:30 3F

Time-resolved Observation and Control of Molecular Vibrations in single-beam CARS — ●BERNHARD VON VACANO and MARCUS MOTZKUS — Physikalisches Chemie, Philipps-Universität Marburg, Hans-Meerwein-Strasse, D-35043 Marburg, Germany

Molecular motion can be measured directly in time-resolved nonlinear Raman spectroscopy, such as coherent anti-Stokes Raman scattering (CARS). Furthermore, using shaped laser pulses, vibrational modes can selectively be excited and the motion of molecules be controlled.[1] The typical drawback of such experiments is their complexity. In the context of microscopy, it has been shown that CARS can successfully and simply be implemented in a single beam of shaped femtosecond laser pulses.[2] In this contribution we show the simultaneous observation and control of molecular vibrations with a single beam of shaped femtosecond laser pulses in the time domain. This technique allows the systematic study of the coherent control of vibrational dynamics,[3] and paves the way for a simple implementation of novel, highly specific schemes in chemical analytics, detection and microscopy based on CARS.

[1] A. M. Weiner, D. E. Leaird *et al.*, *Science* **247**, 1317-1319 (1990)

[2] N. Dudovich, D. Oron, Y. Silberberg, *Nature* **418**, 512-514 (2002)

[3] B. von Vacano, M. Motzkus, *J. Chem. Phys.* **127**, 144514 (2007)

MO 7.4 Di 14:45 3F

Zeitaufgelöste MIR-Spektroskopie und Quantenkontrolle in flüssiger Phase — ●MARCO SCHADE¹, DANIEL WOLPERT², GUSTAV GERBER² und TOBIAS BRIXNER^{1,2} — ¹Institut für Physikalische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg — ²Physikalisches Institut, Universität Würzburg, Am Hubland, 97074 Würzburg

Wir diskutieren, wie die Technik der Quantenkontrolle chemischer Reaktionen in der flüssigen Phase etabliert werden kann, um Produktausbeuten zu erreichen, die für praktische Anwendungen interessant sind. Zur Beobachtung molekularer Prozesse in Flüssigkeiten bietet sich

zeitaufgelöste Spektroskopie im mittleren Infrarot (MIR) an. Durch die spektral deutlich getrennten Schwingungsbanden kann man verschiedene Photoprodukte eindeutig identifizieren und somit strukturelle Veränderungen im Verlauf der Reaktion verfolgen. Wir untersuchen die laser-induzierte Wolff-Umlagerung von 2-Diazo-1-naphthoquinone (DNQ) in Methanol. Die zeitaufgelösten MIR-Messungen zeigen, dass ein vibrationsangeregtes Keten gebildet wird, welches innerhalb von ca. 10 ps in den Vibrationsgrundzustand relaxiert. Mit Hilfe von geformten Laserimpulsen wird die Ausbeute dieses Photoprodukts beeinflusst. Variation des linearen Chirps zeigt, dass die betrachtete Photoreaktion sehr empfindlich auf sogenanntes Intrapulsedumping ist. Adaptive Optimierungen, die als Zielvorgabe die Maximierung der Photoproduktausbeute haben, führen zu Pulsformen, die konsistent mit diesem Mechanismus verstanden werden können.

MO 7.5 Di 15:00 3F

Optimal Control Theory With Restrictions in the Frequency Domain — ●MARKUS KOWALEWSKI, CAROLINE GOLLUB und REGINA DE VIVIE-RIEDLE — Department Chemie, LMU München

We present an approach which combines global optimal control with constraints in the frequency domain. Due to the fact that time and frequency are non-commuting variables applying constraints to both of them is a demanding task. We face this problem with a modified Krotov OCT scheme which introduces frequency filters into the functional description of the OCT formulation. High optimization yields can be reached as well a good convergence behavior. In this sense the developed method can be regarded as an enhancement to existing algorithms [1,2]. With this tool at hand we can simulate optimization tasks in an experimentally realizable parameter range with respect to spectral bandwidth and pulse duration. Selected examples are presented to demonstrate the flexibility and efficiency of the algorithm.

[1] M. Artamonov, T.-S. Ho, H. Rabitz, Chem. Phys. **305**, 213 (2004).

[2] C. P. Koch, J. P. Palao, R. Kosloff, F. M. Seeuws, Phys. Rev. A **70** (2004).

MO 7.6 Di 15:15 3F

Molecular Vibrational Quantum Computing Based on Stimulated Raman Gates — ●CAROLINE GOLLUB, MARKUS KOWALEWSKI und REGINA DE VIVIE-RIEDLE — Department Chemie, LMU München

The concept of molecular vibrational quantum computing [1], is based on vibrational eigenstates encoding the qubits. In a new approach we use stimulated non-resonant Raman processes acting as quantum gates. The advantages of this idea in comparison to IR quantum gates are a higher flexibility in a choice of laser wavelengths in combination with established shaping techniques in the visible and near IR domain. Additionally, chirped pulses might be used as quantum gates. The logic operations can be optimized by a modified Krotov OCT scheme including restrictions on the laser fields in the frequency domain to assure simple pulse spectra. Stimulated Raman gates are presented for a 2D qubit system which is described fully quantum chemically. Additionally, the effects using polarized laser fields are discussed.

[1] C. Tesch, R. de Vivie-Riedle, Phys. Rev. Lett. **89**, 157901 (2002).

MO 7.7 Di 15:30 3F

Verstärken und Steuern von Kohärenzen in einem dissipativen Ozean — ●HEIDE IBRAHIM, MÓNKA HÉJJAS und NIKOLAUS SCHWENTNER — Freie Universität Berlin, Institut für Experimentalphysik, Arnimallee 14, 14195 Berlin

Eine Anregung mit Pulszügen deren Phasen kontrolliert werden, erlaubt das Zusammenführen von zeitlicher und energetischer Selektivität. Nach Testexperimenten mit zwei phasenabgestimmten Pulsen aus einem Michelson Interferometer [1] werden mit einem Pulsformer zeitlich ausgedehntere Pulsfolgen, zur spektral schärferen Anregung im Molekül, erzeugt. Sie sind auf das Schwingungsspektrum des Halogens Brom in einer Edelgasmatrix (Argon) [2] abgestimmt. Zwei Ziele werden dadurch erreicht: Erstens wird ein verschwindend kleiner Anteil einer kohärenten Signatur (B-Zustand) aus einem überragenden inkohärenten Untergrund (A-Zustand) durch Anregung mit kohärenten Pulszügen verstärkt herauspräpariert. Zweitens können durch spektrales Verschieben der Frequenzkammstruktur, welche dem Pulszug entspricht, Matrixphononen angeregt werden. Dies führt zu einer verstärkten oder abgeschwächten Kopplung des B-Zustands mit repressiven Zuständen und somit zu einer Steuerung von Prädissoziation der B-Population. Die verwendeten Pulzüge werden spektral und zeitlich mit Hilfe von Fouriertransformation und Wellenpaketsimulationen bezüglich ihrer Phasen analysiert.

[1]: M. Fushitani, M. Bargheer, M. Gühr, H. Ibrahim und N. Schwentner, J. Phys. B, 2007, eingereicht [2]: H. Ibrahim, M. Gühr und N. Schwentner, J. Chem. Phys. 2007, akzeptiert

MO 7.8 Di 15:45 3F

Von Neumann-Repräsentation zur Darstellung ultrakurzer Laserpulse — ●FRANK DIMLER^{1,2}, SUSANNE FECHNER¹, ALEXANDER RODENBERG^{1,2}, TOBIAS BRIXNER^{1,2}, DAVID TANNOR³ und GUSTAV GERBER¹ — ¹Physikalisches Institut, Universität Würzburg, Am Hubland, 97070 Würzburg — ²Institut für Physikalische Chemie, Universität Würzburg, Am Hubland, 97070 Würzburg — ³Department of Chemical Physics, Weizmann Institute of Science, 76100 Rehovot, Israel

Im Gegensatz zur üblichen Darstellung des elektrischen Feldes im Frequenz- oder im Zeitraum bieten Phasenraumdarstellungen die Möglichkeit, die spektralen und zeitlichen Eigenschaften ultrakurzer Laserimpulse simultan und auf intuitive Weise zu erfassen.

Die von uns vor kurzem eingeführte [1], auf von Neumann zurückgehende Phasenraumdarstellung erlaubt im Gegensatz zu den üblicherweise verwendeten eine vollständige Rekonstruktion des elektrischen Feldes in Amplitude und Phase bei gleichzeitigem Erhalt der intuitiven Interpretierbarkeit.

Wir diskutieren den grundlegenden Formalismus anhand numerischer Beispiele und erklären, welche Frequenz- und Zeitauflösung in einer Phasenraumdarstellung prinzipiell erforderlich sind, um das elektrische Feld vollständig zu rekonstruieren.

[1] Optics Express, Vol. 15 Issue 23, pp.15387-15401

MO 8: Kalte Moleküle I (gemeinsam mit Q)

Zeit: Dienstag 8:30–10:30

Raum: 3G

Hauptvortrag

MO 8.1 Di 8:30 3G

Cold Polar Molecules: From Production to State-Selective Detection — ●PEPIJN W.H. PINKSE, LAURENS D. VAN BUUREN, MICHAEL MOTSCH, MARKUS SCHENK, CHRISTIAN SOMMER, MARTIN ZEPPEFELD, and GERHARD REMPE — Max-Planck-Institut für Quantenoptik, Hans-Kopfermann-Str. 1, 85748 Garching

Cold polar molecules promise opportunities in various research fields such as chemistry, metrology, molecular physics and quantum information processing. To this end, advanced production, trapping and cooling techniques are required.

An overview will be given of the methods developed in our laboratory: we filter slow molecules out of a thermal ensemble by exploiting the Stark effect in polar molecules such as formaldehyde, ammonia and water. The thermal ensemble in the source can be at room temperature or at cryogenic temperature, in which case helium is used as a cold buffer gas. Using suitably shaped electric fields, slow polar

molecules are guided into ultrahigh vacuum, where we can store them in an electric trap.

While the motional energy of the filtered molecules is in the 1K range, the rotational temperature is higher. Depending on the temperature of the source and the molecular constants, many rotational states can be occupied. As a preparation for optical measurements, we performed high-resolution molecular UV spectroscopy on formaldehyde. With the gained information, we can now measure the distribution over the internal states of guided formaldehyde by state-selectively depleting the beam by optical pumping. Precise knowledge over the state distribution will be vital for further cooling down the molecules, for instance by means of an optical cavity.

MO 8.2 Di 9:00 3G

Cryogenic buffer-gas cooling and magnetic trapping of CrH and MnH molecules — ●MICHAEL STOLL¹, JOOST BAKKER², GERARD MEIJER¹, and ACHIM PETERS³ — ¹Fritz-Haber-Institut der Max-

Planck-Gesellschaft, Berlin — ²FOM Institute for Plasma Physics, Rijnhuizen, the Netherlands — ³Humboldt Universität zu Berlin, Institut für Physik

Buffer gas loading of molecules into a cryogenic He-filled cell and magnetic trapping of the thermalized molecules has been proven to be a powerful method for the production of samples of trapped cold molecules.

We report on the successful cooling of MnH and CrH molecules to sub-Kelvin temperatures using a He dilution refrigerator. Subsequently the molecules were loaded into a trapping field generated by a superconducting quadrupole magnet. Storage times of ~ 120 ms could be demonstrated for both molecules.

We modeled the dynamics of our system using a Monte Carlo approach in order to investigate different possible inelastic scattering processes responsible for limitations to the trapping time. Collision cross sections were obtained by fitting this model to the measured diffusion times of both molecules. Combining our system with the already demonstrated methods for rapid extraction of the buffer gas should in principle allow for the preparation of thermally isolated samples with then much longer lifetimes.

MO 8.3 Di 9:15 3G

The electrostatic analogue of a Ioffe-Pritchard trap — ●MORITZ KIRSTE, MELANIE SCHNELL, and GERARD MEIJER — Fritz-Haber-Institut der MPG, Abt. Molekülphysik, Faradayweg 4-6, D-14195 Berlin

By exploiting the Stark effect one can trap polar molecules. In an electric field the molecules separate, due to the Stark effect, in low-field seeking and high-field seeking states, where molecules in low-field seeking states can be confined in the minimum of an electrostatic quadrupole trap. Trapped molecules are useful in the study of dipole-dipole interaction, the alignment of molecules in external fields and for high-resolution spectroscopy. These techniques are limited by the density of trapped molecules, the trap depth, trap frequency and trapping-time. Trap losses arise from inelastic collisions and from Majorana transitions. In electrostatic traps, the Majorana losses can be compensated by the use of an electric analogue to a magnetic Ioffe-Pritchard trap, which generates a trapping field that is non-zero at the center. In this talk we will introduce the first Ioffe-Pritchard like electrostatic trap. We will present our experimental results, characterizing the trap and will sketch its possible applications.

MO 8.4 Di 9:30 3G

Lifetime measurements with electrostatically trapped cold molecules — ●JOOP J. GILJAMSE, STEVEN HOEKSTRA, MARKUS METSÄLÄ, SEBASTIAAN Y.T. VAN DE MEERAKKER, and GERARD MEIJER — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

With a Stark decelerator, bunches of state-selected molecules with a controlled velocity and with longitudinal temperatures as low as a few mK can be produced. These slow bunches of molecules can subsequently be trapped in an electrostatic trap. We will report on the deceleration and trapping of ground state OH, and metastable CO and NH molecules. The OH radicals are trapped at a density of $10^7 - 10^8 \text{ cm}^{-3}$ and at a temperature of around 50 mK, and their trap lifetime is measured to be 2.8 s. The long interaction time afforded by the trap can be exploited to measure lifetimes of vibrationally excited states or electronically excited metastable states. Such lifetimes can be used as an accurate test of theoretical models. We will present experiments on the lifetime of OH ($X^2\Pi_{3/2}, v = 1$) and of metastable CO ($a^3\Pi, v = 0$). The different loss processes that play a role in the trap, like optical pumping by blackbody radiation, were studied in detail.

[1] S. Hoekstra *et al.*, Optical pumping of trapped neutral molecules by blackbody radiation, PRL 98: 133001 (2007)

[2] J.J. Gilijamse *et al.*, The radiative lifetime of metastable CO ($a^3\Pi, v = 0$), J.Chem.Phys. [in press], Arxiv:0710:2240 (2007)

MO 8.5 Di 9:45 3G

Guiding and decelerating polar molecules above a microstructured electrode array — ●SAMUEL A. MEEK, HENDRICK L. BETH-

LEM, HORST CONRAD, and GERARD MEIJER — Fritz-Haber-Institut der MPG, Faradayweg 4-6, 14195 Berlin

The feasibility of manipulating polar molecules by means of inhomogeneous electric fields has been successfully demonstrated by various devices, such as Stark decelerators, electrostatic traps and storage rings. While previous electrode configurations at the mm scale require potential differences of tens of kV at the electrodes, similar fields can be produced between $10\mu\text{m}$ -sized electrodes using potentials of hundreds of volts. Here, we present an electrostatic decelerating and trapping device consisting of a periodic array of 1254 microstructured linear electrodes deposited on a planar glass substrate. Application of harmonic waveforms to periodic groups of six electrodes forms a series of periodic minima which move along the array in a continuous manner without changing their distances above the electrodes. Deceleration is achieved by linearly reducing the frequency of the applied waveforms.

First experiments have been performed using a supersonic beam of $a^3\Pi_1$ CO, which has a lifetime of 2.6 milliseconds. Molecules are excited with a laser directly after the nozzle and later detected using Auger deexcitation at a gold surface. TOF spectra clearly demonstrate the velocity-selective guiding of CO*, with guided velocities proportional to the frequency of the applied waveforms. First results of decelerating the CO* molecules by linearly decreasing the frequency of the waveforms, i.e. velocity of the minima, are also presented.

MO 8.6 Di 10:00 3G

Spatially separating individual conformers of neutral molecules — ●FRANK FILSINGER, UNDINE ERLEKAM, HENRIK HAAK, GERT VON HELDEN, JOCHEN KÜPPER, and GERARD MEIJER — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, Berlin, Germany

Large (bio)molecules exhibit multiple conformers (structural isomers), even under the cold conditions present in a supersonic jet. For various applications, i.e., scattering experiments, it would be highly desirable to prepare molecular packets of individual conformers.

It is well-known that polar molecules can be manipulated using strong electric fields. Many techniques have been developed for the manipulation of small molecules in low-field-seeking quantum states. However, application of these techniques to large molecules is not straightforward, because, for larger molecules, all states are high-field seeking at the relevant electric field strengths. To manipulate the motion of large molecules one has to use Alternate Gradient (dynamic) focusing. This method has been successfully demonstrated in the Alternate Gradient deceleration of CO and YbF. Using the same Alternate Gradient focusing principle, applying switched electric fields in a *quadrupole* guide, we have set up a new experiment to spatially separate individual conformers of large molecules. This experiment exploits the different mass-to-dipole (m/μ) ratios, similar to a quadrupole mass-to-charge (m/q) filter for ions.

In a proof-of-principle experiment, we have demonstrated the conformer selection of cis- and trans-3-aminophenol.

MO 8.7 Di 10:15 3G

Formation of ultracold heteronuclear dimers in electric fields — ●MICHAEL MAYLE¹, ROSARIO GONZALEZ-FEREZ², and PETER SCHMELCHER^{1,3} — ¹Theoretische Chemie, Universität Heidelberg, Im Neuenheimer Feld 229, 69120 Heidelberg — ²Instituto 'Carlos I' de Física Teórica y Computacional and Departamento de Física Atómica Molecular y Nuclear, Universidad de Granada, E-18071 Granada, Spain — ³Physikalisches Institut, Universität Heidelberg, Philosophenweg 12, 69120 Heidelberg

The effects of a strong electric field on the radiative and steric properties of heteronuclear alkali dimers are investigated. In particular, we study the formation of ultracold LiCs molecules via stimulated emission followed by a radiative deexcitation cascade in the presence of a static electric field. By analyzing the corresponding cross sections, we demonstrate the possibility to populate the lowest rotational excitations via photoassociation. The modification of the radiative cascade due to the electric field leads to narrow rotational state distributions in the vibrational ground state. External fields might therefore represent an additional valuable tool towards the ultimate goal of quantum state preparation of molecules.

MO 9: Kalte Moleküle II (gemeinsam mit Q)

Zeit: Dienstag 11:00–13:00

Raum: 3G

MO 9.1 Di 11:00 3G

Deceleration, trapping and accumulation of NH molecules — ●STEVEN HOEKSTRA, MARKUS METSÄLÄ, PETER C. ZIEGER, LUDWIG SCHARFENBERG, JOOP J. GILJAMSE, SEBASTIAAN Y.T. VAN DE MEERAKKER, and GERARD MEIJER — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

We report on the Stark-deceleration and electrostatic trapping of metastable NH molecules. Furthermore, the progress towards higher densities of cold neutral molecules by accumulation of multiple Stark-decelerated packets of NH molecules in a magnetic trap will be presented.

NH molecules in the long-lived metastable $a^1\Delta(v=0, J=2)$ state are ideally suited for Stark deceleration experiments because of their relatively large Stark shift and low mass. The metastable molecules ($\tau > 2.7$ s) are produced in a supersonic expansion with a velocity of ~ 450 m/s, and are decelerated to a standstill by a 108-stage decelerator. Subsequently the metastable molecules are trapped electrostatically, with a temperature of about 50–100 mK, a density of $\sim 10^6$ cm $^{-3}$ and a $1/e$ trapping lifetime of 1.4 s.

Following the deceleration and trapping, the metastable NH molecules are detected by the excitation of a spin-forbidden transition, resulting in spontaneous decay to the electronic ground state ($X^3\Sigma^-$). The electronic ground state has a negligible Stark shift, but can be trapped magnetically. The first experiments on the accumulation of ground state NH molecules in a magnetic trap will be presented.

MO 9.2 Di 11:15 3G

Alternating gradient focusing and deceleration of large molecules — KIRSTIN WOHLFART, ●FABIAN GRÄTZ, FRANK FILSINGER, GERARD MEIJER, and JOCHEN KÜPPER — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany

During the last decade, fascinating progress has been made in the spectroscopy of the “molecular building blocks of life”. Meanwhile, our group has been developing methods to decelerate neutral, polar molecules using time varying inhomogeneous electric fields. Extending these techniques to bio-molecules would allow, for instance, to increase observation times for precision spectroscopy or to separate different conformers. However, for such large molecules all states are practically high-field seeking. Therefore, alternating gradient focusing has to be applied. Here, we demonstrate the focusing and deceleration of benzonitrile (C_7H_5N) from a molecular beam. Benzonitrile is prototypical for large asymmetric top molecules that exhibit rich rotational structure and a high density of states. It is decelerated in its absolute ground state from 320 m/s to 289 m/s, and similar velocity changes are obtained for excited rotational states. We are setting up a longer alternating gradient decelerator, which will enable us to decelerate benzonitrile or larger molecules to much lower velocities and to thereby completely separate the decelerated packet from the rest of the beam pulse.

MO 9.3 Di 11:30 3G

On the Stark effect of NaK — ●ANDREAS GERDES, HORST KNÖCKEL, and EBERHARD TIEMANN — Institut für Quantenoptik, Gottfried Wilhelm Leibniz Universität Hannover, Welfengarten 1, 30167 Hannover

After preliminary measurements in a heatpipe setup [1] and characterization of our new molecular beam apparatus we show the next step of investigation concerning the heteronuclear molecule NaK. A homogeneous electric field in the detection zone will modify the rotational structure of the spectral lines under consideration. For a model description of the line shapes, not only the molecular Stark effect of the absolute ground state $X^1\Sigma^+$ of the molecule, but also the splitting of the excited state $B^1\Pi$ has to be taken into account. Results of our investigation into this direction will be shown. A comparison with theoretical predictions is possible [2]. Prospects heading to the target molecule KRb will be discussed.

[1] A. Gerdes *et al.*, To be published[2] M. Aymar and O. Dulieu, *J. Chem. Phys.* **122** 204302 (2005)

MO 9.4 Di 11:45 3G

Simulations of LiCs spectra — ●ANNA GROCHOLA, JOHANNES DEIGLMAYR, JÖRG LANGE, KARIN MÖRTLBAUER, CHRISTIAN GLÜCK, ROLAND WESTER, and MATTHIAS WEIDEMÜLLER — Albert-Ludwigs Universität, Physikalisches Institut, Hermann-Herder-Str. 3, 79104 Freiburg i.Brs., Germany

Recently the formation of ultracold LiCs molecules was achieved in our group [1] and spectra of resonant enhanced one-color two photon ionization were recorded.

Here we present predictions for photoassociation and REMPI spectra of the LiCs molecule based on theoretical potential energy curves [2-4] and experimental data [5,6]. Hund’s cases (a) and (c) are taken into account. The Franck-Condon factors are calculated for the $B^1\Pi-X^1\Sigma^+$ system for the free-bound and bound-bound transitions. The results of spectra simulations are compared with the experimental results.

[1] S. D. Kraft *et al.*, *J. Phys. B* **39**, S993 (2006)[2] M. Aymar and O. Dulieu, *J. Chem. Phys.* **122**, 204302 (2005)[3] M. Korek *et al.*, *Can. J. Phys.* **78**, 977 (2000)

[4] Dunia Houalla, Master Thesis, Beirut Arab University (2005)

[5] P. Staantum *et al.*, *Phys. Rev. A* **75**, 042513 (2007)

[6] A. Pashov, private communication

MO 9.5 Di 12:00 3G

Triplet spectroscopy on ultracold 87Rb2 molecules — ●FLORIAN LANG¹, GREGOR THALHAMMER^{1,2}, KLAUS WINKLER¹, CHRISTOPH STRAUSS¹, RUDOLF GRIMM^{1,3}, and JOHANNES HECKER DENSCHLAG¹ — ¹Institut für Experimentalphysik und Forschungszentrum für Quantenphysik, Universität Innsbruck — ²LENS European Laboratory for Nonlinear Spectroscopy and Dipartimento di Fisica, Università di Firenze — ³Institut für Quantenoptik und Quanteninformatiön, Österreichische Akademie der Wissenschaften

Starting from a pure sample of ultracold 87Rb2 Feshbach molecules held in a 3D optical lattice we have performed spectroscopic measurements on electronically excited triplet molecules. We investigate the vibrational ladder down to the vibrational ground state with high resolution in the order of 1 MHz and find good coupling strength to the electronic ground state. In combination of our previous results[1],[2] this offers a promising route towards the production of molecules in the triplet ground state. In my talk I will report on the latest progress in our work.

[1] Coherent optical transfer of Feshbach molecules to a lower vibrational state, K. Winkler, F. Lang, G. Thalhammer, P. v.d. Straten, R. Grimm, J. Hecker Denschlag *Phys. Rev. Lett.* **98**, 043201 (2007)

[2] Cruising through molecular bound state manifolds with radio frequency, F. Lang, P.v.d. Straten, B. Brandstätter, G. Thalhammer, K. Winkler, P.S. Julienne, R. Grimm, J. Hecker Denschlag, submitted for publication, arXiv:0708.3958

MO 9.6 Di 12:15 3G

Photoexcitation and photodissociation of H_3^+ — ●DENNIS BING¹, MAX H. BERG¹, HOLGER KRECKEL², ANNEMIEKE PETRIGNANI¹, SASCHA REINHARDT^{1,3}, XAVIER URBAIN⁴, and ANDREAS WOLF¹ — ¹Max-Planck-Institut für Kernphysik, Saupfercheckweg 1, 69117 Heidelberg, Germany — ²Columbia University, 550 West 120th Street, New York, NY 10027, USA — ³Max-Planck-Institut für Quantenoptik, Hans-Kopfermann-Str. 1, 85748 Garching, Germany — ⁴Département de Physique, Université Catholique de Louvain, B-1348, Louvain-la-Neuve, Belgium

We present ro-vibrational laser spectroscopy of cold H_3^+ towards the dissociation limit and photodissociation of vibrationally excited H_3^+ ions, using two distinct experimental setups. The photoexcitation of H_3^+ was performed in a 22-pole radiofrequency ion trap, where the ions were cooled down to their lowest rotational states and then ro-vibrationally excited by ~ 1 eV (~ 5 vibrational quanta), i.e., above the molecule’s barrier to linearity. Transitions of about 11230 - 13330 cm $^{-1}$ were scanned with a Titanium-Sapphire laser, finding lines with predicted Einstein A-coefficients down to $< 10^{-1}$ s $^{-1}$. The photodissociation of H_3^+ was performed in a crossed photon and ion-beam setup using a pulsed frequency-doubled dye laser at 294 nm and H_3^+ ions from a hot ion source. Both dissociation channels, $H_2^+ + H$ and $H^+ + H_2$, were found and investigated.

MO 9.7 Di 12:30 3G

Photodetachment of cold negative ions — ●PETR HLAVENKA, RICO OTTO, SEBASTIAN TRIPPEL, JOCHEN MIKOSCH, MATHIAS WEIDEMÜLLER, and ROLAND WESTER — Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg

With the recent detection of negative carbon clusters in the interstellar molecular clouds, laboratory studies of negative ions are becoming exceedingly important. We study absolute OH^- photodetachment cross sections as a model for the low temperature behavior of this fundamental light-matter interaction, which is a main loss channel of the anions in interstellar medium (ISM). To reach ISM-relevant conditions we study the photodetachment interaction of laser light with anions captured in a 22-pole RF trap [1]. The sympathetic cooling of ions captured in the flat effective potential yields well defined rotational-state distributions. We record the relative loss of stored anions due to the photodetachment while scanning the volume of the trap with a focussed, 2D movable laser beam. A column-density map and the absolute photodetachment cross section are obtained. We present results for OH^- photodetachment at different temperatures and laser wavelengths. This gives insight to the rotational dependence of the photodetachment process, which gives us better understanding of the processes leading to the anion abundances in the ISM.

[1] S. Trippel et al., Phys. Rev. Lett. **97**, 193003 (2006)

MO 9.8 Di 12:45 3G

Trapping and cooling of single molecular ions for time resolved diffraction experiments — ●GÜNTHER LESCHHORN, STEFFEN KAHRA, and TOBIAS SCHAETZ — Max-Planck-Institut für Quantenoptik, Garching

The interest in observing structural changes in molecules with a time resolution of a few femtoseconds and below give rise to discussions about modifying the established target schemes. The Tlamo-project (trapped ions and molecules) aims for an electron or X-ray diffraction experiment using single molecular ions. We report on the progress towards a setup for the preparation of single, cold and well (spatial resolution: $1\ \mu\text{m}$) localized molecular ions, that can be continuously replaced to achieve suitable statistics in a single target experiment. By combining numerous experimental techniques like Paul-traps, sympathetic cooling, light pressure and separation of molecular ions from a Coulomb-crystal using electric fields, it should be possible to achieve a replacement in the kHz-regime. In the future, this scheme together with electron or X-ray diffraction on a single molecular ion can be used to directly observe fast molecular reaction dynamics. Supported by: MAP, IMPRS-APS, MPG

MO 10: Kalte Moleküle III (gemeinsam mit Q)

Zeit: Dienstag 14:00–16:00

Raum: 3G

MO 10.1 Di 14:00 3G

Cumulenic carbon chains: giant absorbers — ●DMITRY STRELNIKOV and WOLFGANG KRÄTSCHMER — Max-Planck-Institut für Kernphysik, 69117 Heidelberg.

Cumulenic carbon chains have extremely strong IR and UV-Vis absorptions, a feature which facilitates their detection even in minute quantities. We present our results obtained by IR and UV-Vis spectroscopy on bare carbon chains and their oxides trapped in cryogenic matrices. IR spectra of a novel hybrid molecule consisting of a C3 carbon chain attached to a C60 fullerene will also be presented and discussed.

MO 10.2 Di 14:15 3G

Internal-state thermometry by depletion spectroscopy in a cold guided beam of formaldehyde — ●MICHAEL MOTSCH, MARKUS SCHENK, LAURENS D. VAN BUUREN, MARTIN ZEPPEFELD, PEPLIJN W.H. PINKSE, and GERHARD REMPE — Max-Planck-Institut für Quantenoptik, Hans-Kopfermann-Str. 1, 85748 Garching, Germany

Velocity filtering by means of an electrostatic quadrupole guide is an efficient technique to produce slow beams of polar molecules from a thermal reservoir. For formaldehyde, fluxes of $10^{10}\ \text{s}^{-1}$ with velocities down to $\sim 10\ \text{m/s}$ have been demonstrated [1]. However, so far the internal-state distribution of the velocity filtered molecules was not accessible in the experiment.

We present measurements of the internal-state distribution of electrostatically guided formaldehyde [2]. Upon excitation with continuously tunable ultraviolet laser light, molecules can be excited to a dissociating state, leading to a decrease in the molecular flux. The population of individual guided states is measured by addressing transitions originating from them. The measured populations of selected states show good agreement with theoretical calculations for different temperatures of the molecule reservoir. The purity of the guided beam as deduced from the entropy of the guided sample using a reservoir temperature of 150 K corresponds to that of a thermal ensemble with a temperature of about 30 K.

[1] S.A. Rangwala et al., Phys. Rev. A **67**, 043406 (2003)

[2] M. Motsch et al., arXiv:chem-phys 0710.3316v1 (2007), accepted for publication in Phys. Rev. A

MO 10.3 Di 14:30 3G

Cooling and Slowing in High Pressure Jet Expansions — ●WOLFGANG CHRISTEN and KLAUS RADEMANN — Institut für Chemie, Humboldt-Universität zu Berlin, Brook-Taylor-Strasse 2, 12489 Berlin

The expression for the mean flow velocity in supersonic beams of ideal gases is extended to include real gas properties. This procedure yields an explicit dependence of the flow velocity on pressure, as observed in recent experiments of free jet expansions [1,2]. Applied to stagnation

conditions slightly above the critical point, the model suggests that seeded high pressure jets might be suitable for slowing down virtually any molecule with high efficiency. Moreover, we discuss the consequence of a pressure-dependent flow velocity v_0 for the speed ratio $S = v_0/\Delta v_{\parallel}$ with respect to collisional cooling and suggest to use the velocity spread Δv_{\parallel} as a more non-ambiguous measure of translational temperature in high pressure jet expansions.

[1] L. W. Bruch, W. Schöllkopf, J. P. Toennies, *J. Chem. Phys.* **117**, 1544 (2002).

[2] W. Christen, T. Krause, K. Rademann, *Rev. Sci. Instrum.* **78**, 073106 (2007).

MO 10.4 Di 14:45 3G

Überschallexpansion von überkritischen Fluiden - Ethen und Propan — ●OLIVER KORUP, KLAUS RADEMANN und WOLFGANG CHRISTEN — Institut für Chemie, Humboldt-Universität zu Berlin, Brook-Taylor-Strasse 2, 12489 Berlin

Mit hochaufgelösten Flugzeitmessungen gepulster Überschallmolekularstrahlen wird die Geschwindigkeitsverteilung von reinem Ethen und Propan als Funktion des Stagnationsdrucks und der Stagnationstemperatur bestimmt. Beide Spezies werden hierzu unter präzise definierten Stagnationsbedingungen [1] ins Vakuum expandiert. Der untersuchte Druck- und Temperaturbereich umfasst den gasförmigen, flüssigen und überkritischen Aggregatzustand. Die Messungen werden durch Untersuchungen zur Clustergrößenverteilung, unter Verwendung der Gegenfeldmethode [2], ergänzt. Ausgangspunkt zu den hier präsentierten Ergebnissen sind vorangegangene Untersuchungen [3] zur überraschend effizienten Kühlung bei der Überschallexpansion von CO und CO_2 , die in dieser Arbeit eine Erweiterung auf größere Moleküle finden.

[1] W. Christen, T. Krause, K. Rademann, *Rev. Sci. Instr.* **78**, 073106 (2007).

[2] J. Bauchert, O.-F. Hagen, *Z. Naturforsch.* **20a**, 1135-1142 (1965).

[3] W. Christen, K. Rademann, U. Even, *J. Chem. Phys.* **125**, 174307 (2006).

MO 10.5 Di 15:00 3G

Competing chemical dynamics in $\text{F}^- + \text{CH}_3\text{Cl}$ — ●RICO OTTO, JOCHEN MIKOSCH, SEBASTIAN TRIPPEL, CHRISTOPH EICHHORN, MATTHIAS WEIDEMÜLLER, and ROLAND WESTER — Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg

Chemical reactions often show a variety of competing reaction mechanisms depending on the energy available. We have studied this for anion molecule nucleophilic substitution ($\text{S}_{\text{N}}2$) reactions [1], which are described by a complex potential energy surface with a submerged barrier and by weak coupling of the relevant rotational-vibrational quantum states.

Here we present results for the anion molecule reaction $F^- + CH_3I$ which we studied in a crossed beam imaging experiment at low energies between 0.3 - 12.5 eV. We have observed three distinct reaction channels which we identified by time of flight analysis of the formed product ions. By mapping the transfer from translational energy into internal vibrational modes we could identify different reaction mechanisms for each of these channels.

[1] J. Mikosch, S. Trippel, C. Eichhorn, R. Otto, U. Lourderaj, J. X. Zhang, W. L. Hase, M. Weidemüller, R. Wester, Science (in press)

MO 10.6 Di 15:15 3G

Nonequilibrium magnesium complexes formed in helium nanodroplets — ●ANDREAS PRZYSTAWIK, SEBASTIAN GÖDE, JOSEF TIGGESBÄUMKER, and KARL-HEINZ MEIWES-BROER — Institut für Physik, Universität Rostock, Universitätsplatz 3, 18051 Rostock

Doping helium droplets with alkaline earth atoms is an interesting tool to investigate the interaction with the superfluid helium. Magnesium is a corner case regarding the degree of solvation in helium [1,2] which may enable the detection of quantized vortices in helium droplets.

In this contribution we add another facet to the discussion. The absorption of helium droplets doped with magnesium atoms is measured with resonant two-photon ionization at different combinations of droplet size and the number of doped Mg atoms. This enables the unambiguous identification of the absorption of an isolated atom inside the droplet centered around 279 nm. When increasing the Mg content of the droplet we find evidence for the formation of metastable, weakly bound Mg complexes. After excitation of such a complex it collapses to a Mg cluster on a timescale of 20 ps.

[1] J. Reho *et al.*, J. Chem. Phys. **112**, 8409 (2000)

[2] Y. Ren and V.V. Kresin, Phys. Rev. A **76**, 043204 (2007)

MO 10.7 Di 15:30 3G

High Resolution Spectroscopy of Acetylene-Furan in Ultracold Helium — ●ANJA METZELTHIN, ÖZGÜR BIRER, and MARTINA HAVENITH — Physikalische Chemie II, Ruhr Universität Bochum, Universitätsstr. 150, D-44780 Bochum

The acetylene-furan system is an interesting benchmark system for the evaluation of hydrogen bonds. Since acetylene is the smallest molecule containing two hydrogens and a π -system it is interesting

to study the influence of a C-H "lone-pair" hydrogen-bond and a CH- π or even a π - π interaction.

The global and local minimum structures have been predicted in a recent study [1]. For the experiment the molecules have been embedded in superfluid helium nanodroplets. The radiation source was a single-resonant OPO with an output power of up to 2.7 W and a resolution of up to $4 \times 10^{-5} \text{ cm}^{-1}$. Helium clusters, which have a temperature of 0.37 K are doped with acetylene (pick-up pressure $1.3 \times 10^{-5} \text{ mbar}$) and furan (pick-up pressure $0.9 \times 10^{-5} \text{ mbar}$) and are then excited with the OPO-radiation. A mass-spectrometer is used to detect the depletion of the cluster beam. With this setup measurements were carried out in the region of the asymmetric stretch vibration of the acetylene. Between 3256 cm^{-1} and 3280 cm^{-1} five acetylene-furan cluster peaks could be detected. Two of these could be assigned to the acetylene-furan dimer. We will present a detailed analysis of the data.

[1] E. Sánchez-García, A. Mardyukov, A. Tekin, R. Crespo-Otero, L.A. Montero, W. Sander, G. Jansen, submitted

MO 10.8 Di 15:45 3G

Molecular Spectroscopy in Superfluid Helium Nanodroplets Created in a Pulsed Even-Lavie Nozzle — ●DOMINIK PENTLEHNER and ALKWIN SLENCZKA — Universität Regensburg, Institut für Physikalische und Theoretische Chemie, 93053 Regensburg, Germany

Pulsed molecular beam sources provide enhanced particle density while the average flux of gas is reduced. Therefore, molecular spectroscopy with pulsed lasers provides a better signal to noise ratio in a pulsed molecular beam than obtained in a continuous beam. One of the most reliable pulsed molecular beam sources developed by U. Even and N. Lavie [1] was tested at low temperatures to produce a pulsed beam of superfluid helium droplets. By the observation of Rayleigh scattering and laser induced fluorescence the pulsed droplet source was characterized. The reliability of the Even-Lavie nozzle as helium droplet source appears to be excellent for repetition rates below 30 Hz. The fluorescence excitation spectra of organic molecules doped into the droplets generated in the pulsed nozzle expansion will be presented.

[1] U. Even, J. Jortner, D. Noy, and N. Lavie, C. Cossart-Magos, J. Chem. Phys. **112** (2000), 8068.

MO 11: Ultrakalte Moleküle (gemeinsam mit Q)

Zeit: Dienstag 16:30–18:00

Raum: 3G

MO 11.1 Di 16:30 3G

Photoassociation of ultracold molecules by shaped femtosecond laser pulses — ●WENZEL SALZMANN¹, TERRY MULLINS¹, SIMONE GÖTZ¹, ROLAND WESTER¹, MAGNUS ALBERT¹, JUDITH ENG¹, MATTHIAS WEIDEMÜLLER¹, FABIAN WEISE², ANDREA MERLI², STEFAN WEBER², FRANZISKA SAUER², MATEUSZ PLEWICKI², LUDGER WÖSTE², and ALBRECHT LINDINGER² — ¹Physikalisches Institut, Universität Freiburg, Herrmann-Herder-Str.3, 79104 Freiburg — ²Institut für Physik, Freie Universität Berlin, Arnimallee 14

We present first experiments on the formation on photoassociation of ultracold molecules with shaped femtosecond laser pulses. In a pump-probe sequence of laser pulses, molecules are produced in their excited state from an ultracold gas of rubidium atoms and subsequently ionized. Molecular ions are mass selectively detected with single ion efficiency. Pulse shaping techniques are used to restrict the pump pulse spectral intensity to address only bound molecular potentials of the first electronically excited state and to suppress atomic losses from the trap due to ionization [1]. The pump-probe detected molecular ion signal shows rich oscillatory dynamics, caused by coherent interactions of molecular electronic dipole with the electric field of the pump pulse [2]. Analysis of the data is accompanied by quantum dynamical simulations which give detailed insight into the pulsed photoassociation process. We further find indications for the formation of molecules in their electronic ground state by spontaneous decay.

[1] W. Salzmann *et al.*, PRA **73**, 023414 (2006)

[2] A. Monmayrant *et al.*, PRL **96**, 103002 (2006)

MO 11.2 Di 16:45 3G

Engineering an all-optical route to ultracold molecules in their vibronic ground state — ●CHRISTIANE P. KOCH¹ and ROBERT

MOSZYNSKI² — ¹Freie Universität Berlin, Institut für Theoretische Physik, Arnimallee 14, 14195 Berlin, Germany — ²Dept. of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland

We propose an improved photoassociation scheme to produce ultracold molecules in their vibronic ground state. Formation of molecules is achieved by short laser pulses in a Raman-like pump-dump process where an additional (near-)infrared laser field couples the excited state to an auxiliary state. The efficiency of population transfer is determined by the shape of the excited state potential; it is dauntingly low for typical potentials. In our proposal, the coupling due to the additional field effectively changes the shape of the excited state potential, allowing for efficient population transfer to $v=0$. Such a field-induced coupling can significantly enhance any short pulse Raman-like process.

MO 11.3 Di 17:00 3G

Photoassociation of ultracold LiCs — ●CHRISTIAN GLÜCK, JÖRG LANGE, JOHANNES DEIGLMAYR, STEPHAN KRAFT, KARIN MÖRTLBAUER, ANNA GROCHOLA, ROLAND WESTER, and MATTHIAS WEIDEMÜLLER — Albert-Ludwigs Universität, Physikalisches Institut, Hermann-Herder-Str. 3, 79104 Freiburg i.Brs., Germany

We recently demonstrated the formation of ultracold LiCs molecules by the trapping light of a double species magneto optical trap [1]. After spontaneous decay into the electronic ground state and one-color two-photon ionization, the molecular ions are detected by a high-resolution time-of-flight mass spectrometer [2].

Here we present the active photoassociation of ultracold LiCs molecules, leading to a significantly increased production rate. Photoassociation resonances in the $B^1\Pi$ potential correlated to the $2S_{1/2}$ - $6P_{3/2}$ asymptote are identified and the ro-vibrational state distribution of the produced ground state molecules is discussed. The perspectives

for the production of LiCs molecules in the absolute ground state are evaluated and future experiments with an ultracold gas of polar LiCs molecules are outlined.

- [1] S. D. Kraft *et al.*, J. Phys. B **39**, S993
 [2] S. D. Kraft *et al.*, to appear in Applied Physics B

MO 11.4 Di 17:15 3G

Towards a BEC of Ground State Molecules — ●JOHANN GEORG DANZL, MATTIAS GUSTAVSSON, ELMAR HALLER, MANFRED MARK, and HANNS-CHRISTOPH NÄGERL — Institut für Experimentalphysik und Forschungszentrum für Quantenphysik, Universität Innsbruck, Innsbruck, Austria

We report on recent progress on optical spectroscopy of ultracold Cs₂ Feshbach molecules. Our ultimate goal is the production of ultracold molecules in the rovibrational ground state of the singlet molecular potential [1] and the production of a BEC of ground state molecules. Coherent state transfer with an efficiency approaching unity should be possible by means of stimulated Raman adiabatic passage (STIRAP) [2]. We plan to apply two consecutive two-photon STIRAP steps where the first step will transfer the molecules from the initial Feshbach state to an intermediate vibrational level near $\nu=70$ of the singlet potential. As part of the first step, we have found several strong bound-bound transitions in the wavelength region 1120 nm to 1130 nm, far off resonance from the atomic D1 and D2 lines.

[1] D. Jaksch, V. Venturi, J. I. Cirac, C. J. Williams, and P. Zoller, Creation of a Molecular Condensate by Dynamically Melting a Mott Insulator, Phys.Rev. Lett. 89, 040402 (2002).

[2] K. Winkler, F. Lang, G. Thalhammer, P. v.d. Straten, R. Grimm, J. Hecker Denschlag, Coherent optical transfer of Feshbach molecules to a lower vibrational state, Phys. Rev. Lett. 98, 043201 (2007)

MO 11.5 Di 17:30 3G

Few-body physics with ultracold Cs atoms and molecules — ●STEVEN KNOOP¹, FRANCESCA FERLAINO¹, MARTIN BERNINGER¹, HARALD SCHÖBEL¹, MICHAEL MARK¹, HANNS-CHRISTOPH NÄGERL¹, and RUDOLF GRIMM^{1,2} — ¹Institut für Experimentalphysik, Universität Innsbruck, Austria — ²Institut für Quantenoptik und Quanteninformation, Innsbruck, Austria

Ultracold atomic gases are versatile systems to study few-body physics because of full control over the external and internal degrees of freedom and the magnetic tunability of the scattering properties using Feshbach resonances. Here we experimentally study three- and four-body physics by investigating ultracold atom-dimer and dimer-dimer collisions with Cs Feshbach molecules in various molecular states and Cs atoms in different hyperfine states. Resonant enhancement of the atom-dimer relaxation rate is observed and interpreted as being induced by a trimer state [1]. For dimer-dimer collisions we have observed an unexpected temperature dependence and a suppression of the collisional loss rate [2].

[1] S. Knoop *et al.*, in preparation [2] F. Ferlaino *et al.*, in preparation

MO 11.6 Di 17:45 3G

Photoassociation spectroscopy in a mixture of ultracold Rb and Yb atoms — NILS NEMITZ, ●FLORIAN BAUMER, FRANK MÜNCHOW, and AXEL GÖRLITZ — Institut für Experimentalphysik, HHU Düsseldorf, Germany

Currently, many groups are pursuing the production of ultracold heteronuclear molecules in the electronic ground state. Among the most fascinating features that such a system would offer are the study of strongly dipolar quantum gases and potentially fundamental precision measurements for suitably chosen molecules.

The goal of our experiment is the formation of molecules through photoassociation of ultracold paramagnetic Rb atoms and diamagnetic Yb atoms. The first step towards this goal is the investigation of one-photon spectroscopy from the atomic ground state of the two atomic species to an electronically excited state of the heteronuclear RbYb molecule.

Here, we report on recent results of photoassociation spectroscopy close to the Rb D1-transition at 795 nm in a combined magneto-optical trap. By detecting the Yb trap loss as a function of the frequency of the photoassociation laser, we are able to observe spectral lines corresponding to several vibrational states and resolve the rotational substructure of the excited RbYb molecule.

The next steps will be photoassociation spectroscopy of conservatively trapped RbYb mixtures and the extension to two-photon photoassociation in order to produce ultracold ground state molecules.

MO 12: Stossprozesse, Energietransfer I (gemeinsam mit A)

Zeit: Donnerstag 8:30–10:30

Raum: 3F

Hauptvortrag

MO 12.1 Do 8:30 3F

Reactions of negative ions at low energy — JOCHEN MIKOSCH, SEBASTIAN TRIPPEL, RICO OTTO, CHRISTOPH EICHHORN, PETR HLAVENKA, MATTHIAS WEIDEMÜLLER, and ●ROLAND WESTER — Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg

Interactions of negative ions with small organic molecules represent model systems for the investigation of reaction dynamics in few-body systems. Their corrugated potential energy landscape, originating in long-range attractive and short-range repulsive forces, requires the coupling of different degrees of freedom for reactions to occur. We have adopted two complementary approaches to study anion-molecule reaction dynamics. Using velocity map imaging in combination with crossed beams at low energy we study the differential cross section of negative ion reactions. For nucleophilic substitution reactions we have observed several distinct reaction mechanisms when varying the collision energy [1]. Reaction rate measurements in a 22pole ion trap have revealed unexpected temperature-dependences at low temperatures. These results are relevant for the understanding of the negative ion abundances in interstellar molecular clouds.

[1] J. Mikosch *et al.*, Science (in press)

MO 12.2 Do 9:00 3F

Manipulation von Protonentransferreaktionen mittels Zustandsselektion — ●FRANZISKA UNGER, LISA PAETOW und KARL-MICHAEL WEITZEL — Fachbereich Chemie, Universität Marburg

Ionen-Molekül-Reaktionen (IMR) sind von großer Bedeutung für zahlreiche natürliche und künstliche Prozesse, insbesondere in der Plasmachemie. Ein wichtiger Vertreter der IMR ist der Protonentransfer (PT), auf dem auch eine der empfindlichsten Methoden der Spu-

renanalytik, die Protonentransfer-Massenspektrometrie, basiert. Diese ermöglicht Nachweisgrenzen im ppt-Bereich. Eine interessante, bisher nicht vollständig verstandene Frage ist die nach dem Einfluss der Rotation auf Reaktionen zwischen Ionen und Molekülen, speziell im Vergleich exothermer und endothermer Reaktionssysteme. Hier beschreiben wir erstmals eine systematische Untersuchung der Wirkungsquerschnitte für den PT von HBr⁺ auf CO₂ (sowie CO) mit Kontrolle des Spin-Bahn-Zustandes und der Molekülrotation des HBr⁺-Ions. Wir zeigen, dass der Wirkungsquerschnitt für ein exothermes Reaktionssystem mit der Stoßenergie abnimmt, für ein endothermes Reaktionssystem nimmt er mit der Stoßenergie im Wesentlichen zu. Für beide Systeme hingegen wird der Querschnitt für rotationskalte Ionen maximal. Mögliche Implikationen für technische Prozesse der Plasmachemie werden diskutiert.

MO 12.3 Do 9:15 3F

Photodissociation in a strong laser field — ●SEBASTIAN TRIPPEL, CHRISTOPH EICHHORN, JOCHEN MIKOSCH, RICO OTTO, MATTHIAS WEIDEMÜLLER, and ROLAND WESTER — Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg

Strong light fields are known to provide adiabatic alignment of molecules in free space [1]. Furthermore, such light fields can be used to control dissociation dynamics of molecules [2]. Here we present results on the photodissociation of CH₃I molecules in a strong infrared laser field of up to 10¹² W/cm². Using velocity map slice imaging we measure the three-dimensional velocity distribution of the iodine photofragment. The images reveal significant changes of the dissociation dynamics with increasing laser intensity. In particular, we find that the light field couples the two spin-orbit states of iodine during the dissociation. In the future, this work will be extended to study bimolecular collisions in the laser field.

- [1] H. Stapelfeldt and T. Seideman, *Rev. Mod. Phys.* **75**, 543 (2003)
 [2] I. Thanopoulos and M. Shapiro, *Phys. Rev. A* **74**, 031401 (2006)

MO 12.4 Do 9:30 3F

Interatomic decay of inner-valence-excited states in clusters — ●KIRILL GOKHBERG, VITALI AVERBUKH, and LORENZ S. CEDERBAUM — Theoretische Chemie, Physikalisch-Chemisches Institut, Universität Heidelberg, INF 229, 69120 Heidelberg, BW

In an isolated atom, excitation of an inner valence electron above the outer valence subshell leads to creation of an autoionizing state decaying by the resonant Auger mechanism. Recently, it has been demonstrated experimentally that in a cluster, the inner-valence-excited states can decay also by an interatomic mechanism which has been called resonant interatomic Coulombic decay (RICD). Here we show that RICD is indeed the leading, but not the only possible interatomic decay mode of the inner-valence excitations in clusters [1]. Using Ne ($2s \rightarrow 3p$) excitation in MgNe cluster as an example, we explore the possible decay mechanisms and draw conclusions on their relative importance and on the nature of the corresponding decay products.

1. K. Gokhberg, V. Averbukh, and L.S. Cederbaum, *J. Chem. Phys.* **124**, 144315 (2006)

MO 12.5 Do 9:45 3F

Druck- und temperaturabhängige Flugzeitmessungen gepulster Argon-Überschallstrahlen: Datenauswertung und Schlussfolgerungen bezüglich Kühlung und Kondensation — ●TIM KRAUSE, KLAUS RADEMANN und WOLFGANG CHRISTEN — Institut für Chemie, Humboldt-Universität zu Berlin, Brook-Taylor-Strasse 2, 12489 Berlin

Vorgänge wie die Abkühlung und Kondensation in einer Überschall-expansion sind bis heute nicht vollständig verstanden. So wurde kürzlich gezeigt [1], dass die Expansion oberhalb des kritischen Punktes zu einer überraschend schmalen Geschwindigkeitsverteilung führen kann. Bei der Charakterisierung stellen gepulste Molekularstrahlen eine zusätzliche Schwierigkeit dar. Daher wurde mittels Variation des Stagnationsdrucks p_0 ($10^2 \text{ kPa} < p_0 < 10^4 \text{ kPa}$) und der Stagnationstemperatur T_0 ($310 \text{ K} < T_0 < 410 \text{ K}$) systematisch deren Wirkung auf die Flugzeitverteilung eines Argonstrahls untersucht. Durch eine präzise Regelung der Zustandsgrößen p_0 und T_0 ist eine hohe Genauigkeit und Reproduzierbarkeit möglich [2]. Die Bestimmung der charakteristischen Parameter, mittlere Strömungsgeschwindigkeit v_0 und Breite der Geschwindigkeitsverteilung $\Delta v_{||}$, des gepulsten Überschallstrahls wird vorgestellt.

[1] W. Christen, K. Rademann, U. Even, *J. Chem. Phys.* **125**, 174307 (2006)

[2] W. Christen, T. Krause, K. Rademann, *Rev. Sci. Instrum.* **78**, 073106 (2007)

MO 12.6 Do 10:00 3F

Dissociative recombination of the lowest rotational states

of H_3^+ — ●ANNEMIEKE PETRIGNANI¹, HOLGER KRECKEL², MAX H. BERG¹, SIMON ALTEVOT¹, DENNIS BING¹, HENRIK BUHR³, MICHAEL FROESE¹, JENS HOFFMANN¹, BRANDON JORDAN-THADEN¹, CLAUDE KRANTZ¹, MARIO B. MENDES¹, OLDRICH NOVOTNY¹, STEFFEN NOVOTNY¹, DMITRY A. ORLOV¹, SASCHA REINHARDT¹, TOBIAS M. SORG¹, JULIA STÜTZEL¹, and ANDREAS WOLF¹ — ¹Max-Planck-Institut für Kernphysik, Saupfercheckweg 1, 69117 Heidelberg, Germany — ²Columbia University, 550 West 120th Street, New York, NY 10027, USA — ³Department of Particle Physics, Weizmann Institute of Science, 76100 Rehovot, Israel

The dissociative recombination (DR) of the lowest rotational states of H_3^+ have been investigated at the storage ring TSR using a cryogenic 22-pole radiofrequency ion trap as injector. The H_3^+ was cooled through buffer gas at $\sim 15\text{K}$ to the two lowest rotational levels, $(J,G)=(1,0)$ and $(1,1)$, of the ortho and para proton-spin symmetries. New high-statistics scans of the DR with a photocathode electron source reveal resonances at electron energies down to the 1-10 meV range with ~ 0.5 -1.5 meV collision-energy resolution. The effect of rotational heating is demonstrated by comparing to the rate of a hot H_3^+ beam from a Penning source. Additionally, the reaction dynamics of the 2-body and 3-body break-up for low collision energies were investigated. Comparisons were made using normal- and pure para- H_2 in the cold injection source.

MO 12.7 Do 10:15 3F

Winkelabhängigkeit in molekularen Aufbruchreaktionen mit langsamen Elektronen — ●S. NOVOTNY¹, H. RUBINSTEIN², H. BUHR¹, O. NOVOTNY¹, J. HOFFMANN¹, M.B. MENDES¹, D.A. ORLOV¹, M.H. BERG¹, S. JAROSHEVICH³, B. JORDAN-THADEN¹, C. KRANTZ¹, M. LANGE¹, M. LESTINSKY¹, A. PETRIGNANI¹, D. SHAFIR², D. ZAJFMAN², D. SCHWALM^{1,2} und A. WOLF¹ — ¹Max-Planck Institut für Kernphysik, Heidelberg — ²Weizmann Institute of Science, Rehovot 76100, Israel — ³Institute of Semiconductor Physics, 630090 Novosibirsk, Russia

Die Fragmentationskinematik positiver Molekülionen beim Einfang langsamer Elektronen, der sogenannten Dissoziativen Rekombination (DR), wurde am Schwerionenspeicherring TSR, Heidelberg, mit Hilfe eines hochauflösenden Fragmentabbedungsdetektors untersucht. Die gleichzeitige Überlagerung zweier unabhängiger, kalter Elektronenstrahlen ermöglichte dabei, sowohl die freiwerdende kinetische Energie als auch die Winkelverteilung der neutralen Fragmente des HD^+ Moleküls auf einem feinmaschigen Gitter zwischen ca. 10 und 80 meV Kollisionsenergie zu bestimmen. Wegen der thermischen Rotationsanregung des HD^+ bei Zimmertemperatur und des resonanten Charakters der DR werden Energiebereiche mit stark variierenden Beiträgen niedrig- und hochrotierender Moleküle zum DR Signal beobachtet. Auch die Anisotropie der DR-Fragmente variiert vergleichbar auf der meV-Skala. Die Stärke der Anisotropie und deren Variation deuten darauf hin, dass die Elektronen- und Kernbewegung des Molekülions eng miteinander gekoppelt sind.

MO 13: Stossprozesse, Energietransfer II (gemeinsam mit A)

Zeit: Donnerstag 11:00–12:15

Raum: 3F

Gruppenbericht

MO 13.1 Do 11:00 3F

High-resolution electron collision spectroscopy of the elementary second-row molecular ions — ●O. NOVOTNY¹, M.H. BERG¹, D. BING¹, H. BUHR^{1,2}, H. FADIL¹, M. FROESE¹, J. HOFFMANN¹, A.S. JAROSHEVICH³, B. JORDAN-THADEN¹, C. KRANTZ¹, M. LANGE¹, M. LESTINSKY¹, M.B. MENDES¹, S. NOVOTNY¹, D.A. ORLOV¹, A. PETRIGNANI¹, S. REINHARDT¹, T. SORG¹, and A. WOLF¹ — ¹Max-Planck-Institut für Kernphysik, Saupfercheckweg 1, D-69117 Heidelberg, Germany — ²Department of Particle Physics, Weizmann Institute of Science, Rehovot 76100, Israel — ³Institute of Semiconductor Physics, 630090 Novosibirsk, Russia

The fundamental molecules composed of atoms from the second row of the periodic table (C,N,O,F) have a rich structure of excited potential curves that can be probed at high energy resolution by observing fragmentation processes following collisions with quasi-monochromatic electrons. Experiments of this type are performed in merged electron and ion beams at the ion storage ring TSR in Heidelberg. Using a cold, photocathode-produced electron beam, experiments on the sys-

tem CF^+ yield rich structure in the collision energy dependence of both dissociative recombination and excitation. Moreover, the final atomic levels reached in the fragmentation can be observed, shedding light on their correlation to the collisionally populated excited molecular potentials.

MO 13.2 Do 11:30 3F

Relativistic and non-relativistic LDA, benchmark results and investigation on the dimers Cu_2 , Ag_2 , Au_2 , Rg_2 . — ●OSSAMA KULLIE — University of Kassel, Department of Natural Science, Institute of Physics

Using two spinor minimax method combined with finite element methods accompanied with extrapolation and counterpoise techniques enable us to obtain relativistic highly accurate results for two atomic molecules. Like in our previous work for the (Hartree-) Dirac-Fock-Slater (DFS) functional approximation, we investigate in this work the density functional approximations of the relativistic and nonrelativistic local-density functional, presenting highly accurate benchmark

results of chemical properties on the dimers of the group 11(Ib) of the periodic table of elements. The comparison with DFS, with experimental and literature's results shows that DFS is better behaved than the other two local functionals.

1-O. Kullie, H. Zhang and D. Kolb, submitted to Chem. Phys.. (2007)
 2-O. Kullie, H. Zhang, J. Kolb and D. Kolb, J. Chem. Phys. **125**, 244303 (2006)

MO 13.3 Do 11:45 3F

Semiclassical treatment of non-Markovian dissipative quantum dynamics — ●WERNER KOCH¹, FRANK GROSSMANN¹, JÜRGEN STOCKBURGER², and JOACHIM ANKERHOLD² — ¹Institut für Theoretische Physik, Technische Universität Dresden, 01062 Dresden — ²Institut für Theoretische Physik, Universität Ulm, Albert-Einstein-Allee 11, 89069 Ulm

Any realistic system is coupled to its environment even if this coupling is very weak. The influence of the environment can result in dissipation of energy as well as decoherence of states in the system. Both effects have to be taken into account to accurately describe the time evolution of a state prepared in the system. A model system for the study of these effects is a single oscillator, linearly coupled to a bath of oscillators with a fixed temperature. The dynamics of the heat bath is treated using the influence functional formalism [1]. We show numerical results for the system under the influence of the heat bath using semiclassical techniques in initial value representation [2]. Issues arising during such calculations are discussed.

[1] Feynman, R. P. & Vernon, F. L.. "The theory of a general quantum system interacting with a linear dissipative system." *Annals of Physics*, no. 24 (1963): 118-173.

[2] Herman, M. F. & Kluk, E.. "A semiclassical justification for the use of nonspreading wavepackets in dynamics calculations." *Chemical Physics*, vol. 91 (1984): 27-34

MO 13.4 Do 12:00 3F

A systematic study of the beta-decay properties — ●IVAN BORZOV¹, JOSE CUENCA-GARCÍA¹, KARLHEINZ LANGANKE¹, GABRIEL MARTÍNEZ-PINED¹, and FERNANDO MONTES² — ¹GSI, Darmstadt, Plankstr. 1, D-64291, Darmstadt, Germany — ²National Superconducting Cyclotron Lab., Michigan State University, East Lansing, MI 48824, USA

A self-consistent approach to the nuclear ground states and spin-excitations based on the local energy-density functional (DF) theory and continuum QRPA is presented. Systematic calculations of the total β -decay rates for the nuclei with charge numbers $Z=24-31, 42-49, 72-78, 82-89$ approaching the possible r-process paths in vicinity of the spherical neutron shells at $N=50, 82, 126$ are calculated and compared with the experimental data. When available, the half-lives obtained on the basis of the Finite Range Droplet Model and the shell model are compared to our results. The effects of our calculated half-lives on the r-process abundances in the $A=90-130$ mass region are explored in r-process simulations.

1.J.J. Cuenca- Garcia, G. Martinez-Pinedo, K. Langanke, F. Nowacki, I.N. Borzov, 2007, *Eur.J.Phys. epja/i2007-10477-3*.
 2.Kurtukian-Nietto T., Benlure J, and GSI Collaboration First access to beta half-lives approaching the r-process path near $N=126$., 2007, (submitted to *Phys. Rev. Lett*); *nucl-ex 0711.0101*.
 3.I.N. Borzov, J.J. Cuenca- Garcia, G. Martinez-Pinedo, K. Langanke, F. Montes, 2007, (submitted to *Nucl.Phys. A*).

MO 14: Cluster

Zeit: Donnerstag 8:30–10:30

Raum: 3G

MO 14.1 Do 8:30 3G

Pulsed Molecular Beams of Nucleobases — ●ADNAN SARFRAZ, KLAUS RADEMANN, and WOLFGANG CHRISTEN — Institut für Chemie, Humboldt-Universität zu Berlin, Brook-Taylor-Strasse 2, 12489 Berlin

Transfer of non-volatile and thermally unstable molecules into the gas phase is important for a variety of applications such as analytical mass spectrometry, optical spectroscopy and thin film growth. Supercritical fluids may be used to dissolve molecules at moderate temperature and pressure conditions. This property can be utilized for the molecular beam expansion of thermally labile molecules without the use of significant heat. Extending our previous work [1] we present mass spectra of five biologically relevant nucleic acids (adenine, guanine, cytosine, thymine, and uracil) in a pulsed molecular beam. The molecules are deposited onto a polycrystalline gold surface and studied using Atomic Force Microscopy as well as Thermal Desorption Spectroscopy.

[1] W. Christen, S. Geggier, S. Grigorenko, K. Rademann, *Rev. Sci. Instrum.* **75**, 5048 (2004).

MO 14.2 Do 8:45 3G

Isomer specific spectroscopy of Benzene-Acetylene aggregates — ●MATTHIAS BUSKER, THOMAS HÄBER, MICHAEL NISPEL, and KARL KLEINERMANN — Institut für Physikalische Chemie und Elektrochemie I, Heinrich Heine Universität Düsseldorf, Germany

The relatively strong $CH-\pi$ interactions in Benzene-Acetylene cocrystals have found broad interest due to their importance for the stabilization of supramolecular aggregates, crystal packing, molecular recognition and folding of proteins. We present new gas phase results on medium-sized clusters of Benzene(B) with Acetylene(A) by using mass-resolved Resonant Two Photon Ionisation (R2PI) and IR-UV double resonance spectroscopy for analysis. For BA_{1-2} analysis see A. Fujii, S. Morita, M. Miyazaki, T. Ebata and N. Mikami, *J. Phys. Chem. A*, 2004, 108, 2652. The investigated B_1A_{1-4} and B_2A_{1-2} aggregates were structurally assigned based on comparison of their infrared spectra with ab initio calculated frequencies and intensities and by taking the shift of their electronic spectra into account. The obtained cluster structures were compared with the basic structural units of BA 1:1 cocrystals obtained via x-ray analysis (see R. Boese, T. Clark and A. Gavezzotti, *Helvetica Chimica Acta*, 2003, 86, 1085)

MO 14.3 Do 9:00 3G

What microwave spectroscopy tells us about the benzene dimer — ●UNDINE ERLEKAM¹, MELANIE SCHNELL¹, GERARD MEIJER¹, GERT VON HELDEN¹, JENS-UWE GRABOW², and PHILIP R. BUNKER³ — ¹Fritz-Haber-Institut der MPG, Berlin, Germany — ²Institut für Physikalische Chemie, Leibniz-Universität, Hannover, Germany — ³Steeacie Institute for Molecular Sciences, NRC, Ottawa, Canada

The benzene dimer is a model system for investigating dispersive intermolecular interactions between aromatic molecules. Numerous theoretical and experimental studies exist. Infrared and Raman spectra show different signatures for the two benzene rings in the dimer from which it can be concluded that they are symmetrically inequivalent. Different theoretical calculations find two different minimum structures for the benzene dimer. One is a "parallel-displaced" structure, and the other a distorted T-shaped one with "stem" and "top" benzene rings. The former structure has symmetrically equivalent rings, whereas the latter has symmetrically inequivalent rings in agreement with the Infrared and Raman studies.

We try to solve this conflict using microwave spectroscopy in the 3 to 6 GHz range. In agreement with the only previous microwave study we find a group of microwave transitions, which fit a symmetric top Hamiltonian. It consists of a quartet fine structure with a characteristic intensity and splitting pattern. To explore the origin of this splitting we have studied the microwave spectrum of the $(C_6H_6)_2$ and $C_6H_6-C_6D_6$ isotopologs. Our experimental results will be presented and discussed in the light of the nuclear spin statistics.

MO 14.4 Do 9:15 3G

Pure rotational spectra of PbSe and PbTe: potential function, Born-Oppenheimer breakdown, field shift effect and magnetic shielding — BARBARA M. GIULIANO¹, LUCA BIZZOCCHI¹, STEPHEN COOKE², DEIKE BANSER³, MAREIKE HESS³, JULIANE FRITZSCHE³, and ●JENS-UWE GRABOW³ — ¹Università di Bologna, Dipartimento di Chimica "G. Ciamician", vie F. Selmi 2, 40126 Bologna, Italia — ²University of North Texas, Department of Chemistry, Denton, TX 76203, United States of America — ³Gottfried-Wilhelm-Leibniz-Universität, Institut für Physikalische Chemie & Elektrochemie, Lehrgebiet A, Callinstraße 3A, 30167 Hannover, Deutschland

We present the supersonic-jet Fourier-transform microwave spectra of 42 isotopologues of PbSe (16) and PbTe (26). Using our LASER-ablation jet source, vibrationally very highly excited states of up to

$v=13$ could be prepared. A multi-isotopologue analysis yields precise spectroscopic constants and Born-Oppenheimer breakdown correction coefficients. A significant contribution to the Born-Oppenheimer break-down could be attributed to the finite size of the Pb nucleus, the so-called field-shift effect. From the magnetic hyperfine interaction in isotopologues containing dipolar nuclei the nuclear spin-rotation coupling constants and NMR shielding parameters were determined. Direct fits of a radial Hamiltonian yield analytic potential-energy and Born-Oppenheimer breakdown radial functions. Besides contributing to the understanding of the internuclear potential, electronic structure and chemical bond of intermetallic species, the study also demonstrates the wealth of information encoded in pure rotational spectra.

MO 14.5 Do 9:30 3G

IR spectroscopy on isolated cobalt-alcohol cluster anions — ●PHILIP BIALACH¹, MARTIN WEILER¹, MICHAELA BRAUN², ARNE LÜCHOW², and MARKUS GERHARDS¹ — ¹TU Kaiserslautern, Fachbereich Chemie, Schrödingerstr. 52, 67663 Kaiserslautern & H.-Heine Uni Düsseldorf, Institut für Physikalische Chemie I, 40225 Düsseldorf — ²RWTH Aachen, Institut für Physikalische Chemie, Landoltweg 2, 52056 Aachen

As an example of a model system for investigating metal-anion/ligand compounds we report on clusters of cobalt and alcohols, e.g. methanol, ethanol and propanol. There are questions in understanding the change in physical and chemical properties with increasing cluster size. The metal anions are produced by laser ablation and the alcohols are attached in a supersonic beam. By applying IR-photodetachment or photofragment spectroscopy the OH stretching vibrations of mass-selected cobalt/*n*/alcohol/*m*/ cluster anions (*n*,*m* = 1-3, alcohol=methanol, ethanol, propanol) are investigated. By comparing the experimental results with predictions of ab initio and DFT calculations structural assignments can be obtained. Both the orientation of the OH groups with respect to the metal clusters as well as the orientation of the aliphatic side chains of the alcohols can be discussed.

MO 14.6 Do 9:45 3G

Study of autodetachment effects in the photoemission of fullerene anions — ●MATTIAS SVANQVIST, RAPHAEL KUHNEN, CHRISTINE WEHRSTEIN, and BERND V. ISSENDORFF — Fakultät für Physik, Universität Freiburg, Stefan Meier Straße 21, 79104 Freiburg

The electronic valence structure of fullerenes is determined by the delocalized π -band which can be seen as a spherical two-dimensional electron gas. This makes fullerenes interesting model systems for the study of excitation and relaxation processes in a highly correlated many-electron systems.

In photoelectron spectra of C_{60}^- irradiated by ns-laserpulses evidence of electron Auger-like auto-detachment processes have been observed¹. To verify this peak in the photoelectron spectra as indeed originating from an auto-detachment processes we have conducted a detailed study by scanning a wavelength range of 266 to 322 nm. This shows a linear dependence of the peak position in the binding energy spectras on the photon energy, as expected for auto-detachment, and allows to determine the excitation energy of the autodetaching state as about 3.5 eV.

¹X.-B. Wang et al, J. Chem. Phys. **110**, 8217 (1999)

MO 14.7 Do 10:00 3G

Oberflächenstreuung massenselektierter Molekülcluster: CO_n^+ und $(CO_2)_n^+$ — ●MUHAMMER BULAT, KLAUS RADEMANN und WOLFGANG CHRISTEN — Institut für Chemie, Humboldt-Universität zu Berlin, Brook-Taylor-Strasse 2, 12489 Berlin

Schwach gebundene Cluster aus Molekülen können durch Stöße mit Oberflächen effektiv angeregt werden. Diese Anregungsenergie kann zur Fragmentation des Clusters führen. In einigen Fällen konnten auch stoßinduzierte Intraclusterreaktionen beobachtet werden [1]. Wir stellen Massenspektren für die größten- und energieabhängige Streuung der Molekülcluster CO_n^+ und $(CO_2)_n^+$ vor. Die Cluster werden durch Überschall-expansion erzeugt und mittels Elektronenstoß ionisiert. In einem Reflektoren-Flugzeitmassenspektrometer ($m/\Delta m > 2000$) erfolgt die Beschleunigung ($U_0 \leq 6$ kV) und Größenselektion (Separationsvermögen > 200) der Clusterionen [2]. Durch Variation der Reflektorspannung können die Cluster an dessen letzter Elektrode (Edelstahl) gestreut werden. Die Massenanalyse der bei der Streuung entstandenen Produktionen erfolgt über deren Flugzeit von der Edelstahloberfläche bis zum Detektor. Interessant ist das beobachtete Fragmentationsverhalten der untersuchten Moleküle: Im Gegensatz zu protonierten Clustern (z.B. Ammoniak, Methanol oder Wasser), die bei der Oberflächenstreuung eine Mehrfachfragmentation zeigen, wird bei CO und CO₂ eine sequentielle Fragmentation beobachtet.

[1] W. Christen, U. Even, *J. Phys. Chem. A* **102**, 9420 (1998).

[2] W. Christen, K. Rademann, *Rev. Sci. Instrum.* **77**, 015109 (2006).

MO 14.8 Do 10:15 3G

Lokalisation von K-Schalen-Photoelektronen und ICD-Elektronen in Neondimeren — ●K. KREIDI^{1,2}, T. JAHNKE¹, T. WEBER³, T. HAVERMEIER¹, R. GRISENTI¹, X.-J. LIU⁴, Y. MORISITA⁵, S. SCHÖSSLER¹, L. SCHMIDT¹, M. SCHÖFFLER¹, M. ODENWELLER¹, N. NEUMANN¹, L. FOUCAR¹, J. TITZE¹, B. ULRICH¹, F. STURM¹, C. STUCK¹, R. WALLAUER¹, S. VOSS¹, I. LAUTER¹, H.-K. KIM¹, M. RUDLOFF¹, H. FUKUZAWA⁴, G. PRÜMPER⁴, N. SAITO⁵, K. UEDA⁴, A. CZASCH¹, O. JAGUTZKI¹, H. SCHMIDT-BÖCKING¹, S. K. SEMENOV⁶, N.A. CHEREPKOV⁶ und R. DÖRNER¹ — ¹Institut für Kernphysik, J. W. Goethe Universität, Max-von-Laue-Str. 1, 60438 Frankfurt, Germany — ²DESY, Notkestrasse 85, 22607 Hamburg, Germany — ³Lawrence Berkeley National Laboratory, Berkeley CA 94720, USA — ⁴Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan — ⁵National Metrology Institute of Japan, AIST, Tsukuba 305-8568, Japan — ⁶State University of Aerospace Instrumentation, 190000 St. Petersburg, Russia

Mit der COLTRIMS-Technik wurde der Zerfall von Neondimeren nach der K-Schalen Ionisation mit einer Photonenenergie von 881.2 eV untersucht. Dabei wurden sowohl die Ionen als auch die Elektronen mit einem Raumwinkel von 4π gemessen. Am Aufbruch des Moleküls in die Fragmente Ne^+ und Ne^{2+} wurde die Lokalisation der Photoelektronen sowie der ICD-Elektronen untersucht. Betrachtet wurde hierfür die Winkelverteilung dieser um die Molekülachse.

MO 15: Experimentelle Techniken

Zeit: Donnerstag 11:00–12:15

Raum: 3G

MO 15.1 Do 11:00 3G

Epi-Detected Multiplex CARS Microscopy — ●ANKE HORNEBER, BERNHARD VON VACANO, CHRISTOPH POHLING, and MARCUS MOTZKUS — Physikalische Chemie, Philipps-Universität Marburg, D-35032

Chemically highly sensitive Coherent anti-Stokes Raman Scattering (CARS) spectroscopy can be achieved with a broadband multiplex technique. A single femtosecond laser source produces a narrow pump and probe pulse as well as a broadband Stokes pulse in a photonic crystal fibre. Multiplex CARS allows rapid recording of complete spectra within a vibrational range of more than 2000 cm^{-1} . Using the spectral fingerprint of materials this sensitive method distinguishes clearly between chemically different samples. [1] In our new implementation the generated M-CARS signal is detected in backward direction (Epi) [2], spectrally resolved (better than 60 cm^{-1}) and separated from the ex-

citing laser light by an optimized steep edge bandpass filter. Detection in backwards direction allows mapping of non-transparent samples. It also promises higher three-dimensional spatial resolution and suppression of non-resonant background of bulk solvents. This technique has been successfully applied to map and identify different samples including polymers.

[1] B. von Vacano, L. Meyer, M. Motzkus, *J. Raman Spectroscopy* **38**, 916 (2007).

[2] J. Cheng, A. Volkmer, L. D. Book, X. S. Xie, *J. Phys. Chem. B* **105**, 1277 (2001).

MO 15.2 Do 11:15 3G

Surface Enhanced Raman Scattering (SERS) on Lithographically Fabricated Nano-Structured Gold Surfaces — ●MALTE SACKMANN, TORSTEN BALSTER, VEIT WAGNER, and ARNULF MATERNY — Jacobs University Bremen, Germany

Raman spectroscopy is an optical technique for the characterization of the unique vibrational properties of molecules and therefore is used for chemical analysis. Since the intensity of the inelastically scattered light is weak, this technique is limited to the measurement of higher analyte concentrations in the range of mMol. Surface-enhanced Raman scattering (SERS) provides a possibility to overcome this restriction. By measuring the Raman signal of the molecules in the vicinity of nano-structured surfaces the signal can be enhanced by a factor of 10^6 or more, and therefore concentrations below Mol are detectable.

In order to gain a better understanding of the enhancement mechanisms, we created reproducible, well defined gold dot arrays on a silicon surface via e-beam lithography. The parameters like dot size, thickness, and spacing were varied and the dependence of the enhancement factors on these parameters are investigated. In our contribution we discuss the results of these measurements. With crystal violet (CV) as analyte using the excitation wavelengths 514 and 671 nm enhancement factors up to three orders of magnitude are observed. The SERS substrates were more efficient for the red excitation wavelength by a factor of approx. 10. In our discussion special emphasis is put on the excitation of and coupling to the surface plasmons.

MO 15.3 Do 11:30 3G

Femtosekunden-Polarisationsformung im UV — REIMER SELLE^{1,2}, PATRICK NUERNBERGER^{1,2}, ●FLORIAN LANGHOJER^{1,2}, FRANK DIMLER^{1,2}, SUSANNE FECHNER^{1,2} und TOBIAS BRIKNER^{1,2} — ¹Institut für Physikalische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg — ²Physikalisches Institut, Universität Würzburg, Am Hubland, 97074 Würzburg

Polarisationsgeformte Laserimpulse erlauben es, die vektoriellen Eigenschaften der Licht-Materie-Wechselwirkung gezielt auszunutzen, was insbesondere für die Steuerung stereochemischer Reaktionen von großem Interesse ist. Die anregenden Laserimpulse müssen dabei in einem Spektralbereich liegen, in dem die zu untersuchenden Moleküle absorbieren. Wir präsentieren einen Aufbau und Messungen zur Erzeugung und Charakterisierung von polarisationsgeformten Laserimpulsen im UV Bereich um 400 nm. Dabei kommt ein Polarisationspulsformer mit Volume Phase Holographic Gratings zum Einsatz, welche eine annähernd polarisationsunabhängige Effizienz haben. Die beiden geformten Polarisationskomponenten der 800 nm Impulse werden in einer kollinearen Anordnung von zwei nichtlinearen Kristallen frequenzverdoppelt. Die so erzeugten Pulse werden mit Hilfe von spektraler Interferometrie (in Kombination mit FROG und XFROG) in beiden Polarisationskomponenten gleichzeitig charakterisiert. Die Methode erlaubt es u.a., Doppelpulse und Pulszüge gezielt zu erzeugen, die z.B. für Pump-Probe oder Pump-Dump Experimente eingesetzt werden können.

MO 15.4 Do 11:45 3G

Effizienzmessungen für die Emission der zweiten Excimerkontinua der reinen Edelgase bei Elektronenstrahlanregung

— ●THOMAS HEINDL¹, REINER KRÜCKEN¹, ANDREI MOROZOV¹, ANDREAS ULRICH¹ und JOCHEN WIESER² — ¹Physik Department E12, Technische Universität München, James-Frank-Str. 1, 85748 Garching — ²Coherent GmbH, Zielstattstr. 32, 81379 München

Die Anregung dichter Edelgase mit niederenergetischen (typ. 12keV) Elektronenstrahlen führt zu intensiver Emission der sogenannten 2. Excimerkontinua im Vakuumultraviolett (VUV). Mit den Edelgasen Helium bis Xenon können auf diese Art Lichtquellen mit Emissionswellenlängen von 60 bis 200nm realisiert werden (1). Diese Lichtquellen werden z.B. zur Photoionisation in Massenspektrometern eingesetzt (2). Sie weisen hohe Effizienzen auf. Die Effizienz η wird als Quotient der VUV Strahlungsleistung (in 4π) und der vom Elektronenstrahl im Gas deponierten Leistung definiert. Es werden Messungen vorgestellt, bei denen erstmals für Ne, Ar, Kr und Xe für die Emission der 2. Kontinua bei Elektronenstrahlanregung mit hoher Genauigkeit mit einem absolut kalibrierten Halbleiterdetektor bestimmt wurde. Folgende Werte wurden ermittelt: $\eta_{\text{Ne}}=(0,31\pm 0,10)$, $\eta_{\text{Ar}}=(0,32\pm 0,06)$, $\eta_{\text{Kr}}=(0,42\pm 0,08)$ und $\eta_{\text{Xe}}=(0,42\pm 0,08)$. Die gute Reproduzierbarkeit und der kompakte Aufbau legen die Verwendung als Transferstandard für VUV-Lichtmessungen nahe.

Gefördert durch BMBF 13N8819 und dem MLL.

(1) J. Wieser et al., Rev. Sci. Instrum. 68, 1360 (1997)

(2) F. Mühlberger et al., Anal. Chem. 77, 7408 (2005)

MO 15.5 Do 12:00 3G

Current status of the Cryogenic Trap for Fast Ion Beams and the Cryogenic Storage Ring — ●MICHAEL FROESE¹, MICHAEL LANGE¹, DMITRY ORLOV¹, ROBERT VON HAHN¹, MANFRED GRIESER¹, ANDREAS WOLF¹, MICHAEL RAPPAPORT², and DANIEL ZAJFMAN² — ¹Max-Planck-Institut für Kernphysik, 69117 Heidelberg, Germany — ²Weizman Institute of Science, Rehovot, 76100, Israel

A Cryogenic electrostatic Trap for Fast ion beams (CTF) is being built to develop the technology and techniques necessary to construct the Cryogenic Storage Ring (CSR) for heavy ions in Heidelberg. In both devices, the electrodes and the vacuum chambers they are housed in will be cooled to temperatures between 2-10 K in order to reduce thermal radiation transfer to the stored ions, thereby allowing radiative cooling of molecular ions to the rovibrational ground state. Additionally, storage times on the order of minutes will be made possible by the reduced residual gas pressure in the cryogenic beam pipe (around 10^{-15} mbar). Following commission, the CTF will allow the testing of cryogenic electrostatic ion trapping in extreme vacuum and the development and evaluation of beam diagnostics and particle detectors in a temperature range between 2 and 600 K for the CSR. The techniques employed in the CTF include, for example, the precise, low-thermal-conduction wire suspension of the cold inner vacuum chamber and its in-situ bakeout for minimal gas pressure, and the passage and thermal anchoring of all electrical connections and mechanical actuators through the two layers of thermal shields in the isolation vacuum. The current status of both devices will be presented.

MO 16: Biomoleküle

Zeit: Dienstag 14:00–19:00

Raum: Poster C1

MO 16.1 Di 14:00 Poster C1

Raman Spectroscopy Discrimination of HaCaT and A5RT3 Human Skin Model Cell Lines — ●PATRICE DONFACK, MAREN REHDE, KLAUDIA BRIX, and ARNULF MATERNY — Jacobs University Bremen, Germany

HaCaT and its tumorigenic counterpart A5RT3 cell lines represent good models for studying human skin keratinocytes and carcinoma derived from them. Traditional detection methods of tumor cells relying on immunoblotting are time-consuming. Optical methods are potentially much faster. Fluorescence imaging focuses on the characterization of already known differentiation or dedifferentiation markers. However, Raman spectroscopy (RS) is capable of yielding fingerprint-like characterization of the sample without the necessity of restricting the analysis to few molecules of interest. In our contribution we show the application of RS and surface enhanced RS (SERS) to distinguish between normal HaCaT and tumorigenic A5RT3 cells. Striking differences were revealed in the overall Raman intensity as well as the intensity ratio of the protein amide I band at 1657 and the CH₂ deformation band at 1447 cm⁻¹. These changes were even further pronounced

in the SERS experiments. Lipids are more effective Raman scatterers than proteins. The relatively stronger enhancement of the CH₂ deformation band points to a significantly different lipid content in HaCaT. Furthermore, A5RT3 cells showed higher nucleus/cytoplasm ratios with prominent DNA vibrations and a higher but partly altered protein contribution indicating modifications of cellular metabolism and differentiation state.

MO 16.2 Di 14:00 Poster C1

Single-molecule spectroscopy on low-light adapted light-harvesting 2 complexes of *Rhodospseudomonas palustris* — ●PAUL BÖHM¹, TATAS BRODOSUDARMO², SILKE OELLERICH¹, RICHARD COGDELL², and JÜRGEN KÖHLER¹ — ¹Experimental Physics IV and Bayreuth Institute of Macromolecular Research (BIMF), University of Bayreuth — ²Division of Biochemistry and Molecular Biology, Institute of Biomedical and Life Sciences, Biomedical Research Building, University of Glasgow

Low temperature (1.4 K) single-molecule fluorescence-excitation spectra have been recorded for a novel low-light (LL) adapted light-

harvesting 2 (LH2) complex from *Rhodospseudomonas palustris*. For bulk samples the main spectroscopic feature of this complex in the near infrared is a ratio of 2.9 between the absorption maxima at 800 nm and 850 nm. All studied individual complexes feature 2-3 broad absorption bands in the 840-870 nm spectral region revealing a characteristic polarization dependence. In the 800 nm region the spectra of the individual complexes show several narrow absorption lines which vary from complex to complex both with respect to the number of lines and spectral positions. These measurements may contribute to the elucidation of the electronic structure of this novel light-harvesting complex, as to the narrow lines in the 800 nm region could indicate localized excitations on one or a few B800 bacteriochlorophyll *a* molecules, whereas the broad bands in the 850 nm region may suggest that the excitations are delocalized over a large number of B850 bacteriochlorophyll *a* molecules.

MO 16.3 Di 14:00 Poster C1

Pigment-Pigment Interactions in Light-Harvesting Complexes Investigated by Nonlinear Laser Spectroscopy — ●ALEXANDER BETKE¹, BERND VOIGT¹, ROGER G. HILLER², MARIA KRIKUNOVA³, HEIKO LOKSTEIN⁴, and RALF MENZEL¹ — ¹Institut für Physik/Photonik, Universität Potsdam, Germany — ²Macquarie University, School of Biological Sciences, Australia — ³Institut für Experimentalphysik, Universität Hamburg, Germany — ⁴Institut für Biochemie und Biologie, Universität Potsdam, Germany

Two-photon fluorescence excitation- and nonlinear polarization spectroscopy in the frequency domain (NLPF) are sensitive methods to study pigment-pigment interactions in photosynthetic light-harvesting complexes (LHCs). Among the studied complexes are the peridinin-chlorophyll *a* - protein (PCP) and higher plant LHC II. Interactions between the peridinins and peridinin-chlorophyll interactions in PCP are resolved in the NLPF spectra. Excitonic interactions between the peridinins are revealed. Certain peridinin(s) show interaction between their "optically dark" S_1 ($2^1A_g^-$) or intramolecular charge-transfer state and chlorophyll *a*. Thus, these states are approximately isoenergetic. Two-photon absorption of zeaxanthin and violaxanthin in LHC II monitored by chlorophyll fluorescence shows spectral differences of their "optically dark" $2^1A_g^-$ states. Specific changes in xanthophyll-chlorophyll interactions upon aggregation of LHC II are indicated by NLPF. These changes may underlay the chlorophyll-fluorescence quenching as the molecular basis of excess energy dissipation. Consequences for energy transfer in these complexes are discussed. Supported by the SFB 429.

MO 16.4 Di 14:00 Poster C1

Ion-induced radiation damage to DNA-building blocks — FRESIA ALVARADO, JOS POSTMA, SADIA BARI, PRZEMEK SOBOCINSKI, RONNIE HOEKSTRA, and ●THOMAS SCHLATHÖLTER — KVI Atomic Physics, University of Groningen, The Netherlands

The interaction of keV protons and heavy ions with DNA building blocks is of particular biological relevance in view of the increasing number of facilities employing MeV proton/heavy-ion irradiation for tumor treatment. When these ions traverse tissue and are decelerated to sub MeV energies, the so-called Bragg-peak is reached where the induced damage is highest due to maximum linear energy transfer (LET) and relative biological effectiveness (RBE) at these energies. Biological consequences of irradiation with energetic protons and heavy ions from galactic cosmic rays (GCR) and solar particle events (SPE) are also a limiting factor for human space exploration.

We investigate the response of isolated DNA building blocks and their clusters upon keV singly and multiply charged ion impact using high resolution coincidence time-of-flight mass spectrometry. Fragment ion energies exceeding several 10 eV are observed which have the potential to induce subsequent damage in a biological environment. Deoxyribose molecules from the DNA backbone are found to be most sensitive to keV ion impact and thus represent the weakest link in the DNA structure. Comparative studies on isolated molecules and molecules embedded in clusters reveal that intermolecular hydrogen bonds strongly affect the fragmentation dynamics of the DNA building blocks under study.

MO 16.5 Di 14:00 Poster C1

IR Spectroscopy of self-associated adenine derivatives — ●LARS BIEMANN¹, THOMAS HÄBER¹, DANIELA MAYDT², KLAUS SCHAPER², and KARL KLEINERMANN¹ — ¹Institut für Physikalische Chemie, Heinrich-Heine Universität Düsseldorf, 40225 Düsseldorf, Germany — ²Institut für Organische Chemie, Heinrich-Heine Universität Düsseldorf, 40225 Düsseldorf, Germany

Self-association of 9-substituted adenine derivatives were investigated via IR-spectroscopy in CDCl₃ solutions. The infrared spectra of 9-ethyladenine and N-methyl-9-ethyladenine and its aggregates are presented in the mid and near IR spectral regions. Wavelength dependent absolute extinction coefficients of the monomer and dimers are presented on the basis of a simple deconvolution method which is explained in detail. Comparison of the deconvoluted dimer spectra with quantum chemical calculations allows for a structural assignment of the two dimer structures that coexist in 9-ethyladenine/CDCl₃ solutions. In contrast, the dimer spectrum of N-methyl-9-ethyladenine is dominated by a single isomer.

MO 16.6 Di 14:00 Poster C1

The Influence of Seasonal Changes of the Day-Night Rhythm on the Composition of Hamster Bones Investigated by Raman Spectroscopy — ●JING SHEN^{1,2}, JIMING HU², ALEXANDER LERCHL¹, and ARNULF MATERNY¹ — ¹Jacobs University Bremen, Germany — ²Wuhan University, China

Raman spectroscopy is a non-destructive method, which can provide vibrational information on molecular level for biomedical samples. The change of the light and dark phases (photoperiods) considerably influences the vital functions of Djungarian hamsters. For example, it has been proven that a winter-time photoperiod results in a decline of body weight and is associated with changes of the gonadal function and fur color [1]. In our study, Raman spectroscopy is applied to observe bone compositional differences between long- (16L:8D) and short-day (8L:16D) photoperiod Djungarian hamsters. The bones were cut perpendicularly to the diaphysis at the condyle and in the middle of the diaphysis in order to have access to both cortical bone and trabeculae. Spectra were obtained from different points of each sample and were then averaged. Our results demonstrate that long-day cortical bone samples have a higher phosphate-to-carbonate ratio in both femur and tibia.

[1] A. Lerchl *et al.*, *Neuroendocrinology* **57**,359 (1993).

MO 16.7 Di 14:00 Poster C1

Time-Resolved Spectroscopy on Molybdo Iron-Sulfur Flavoproteins — ●FLORIAN SPREITLER¹, ASTRID PELZMANN², ORTWIN MEYER², and JÜRGEN KÖHLER¹ — ¹Experimentalphysik IV and BIMF, Universität Bayreuth, Universitätsstraße 30, 95447 Bayreuth, Germany — ²Mikrobiologie, Universität Bayreuth, Universitätsstraße 30, 95447 Bayreuth, Germany

Flavoproteins are of great importance in nature because they function in several life-sustaining processes, such as cellular respiration, redox biochemistry, purine metabolism and the oxidation of CO. Their common cofactor flavin adenine dinucleotide (FAD), which can be bound in a covalent or non-covalent fashion, is thought to be fine-tuned by the respective protein matrix both in its redox properties and the exposure of certain atoms to the solvent.

Our main objective is to study the fast photophysics of FAD in different enzymes and enzyme mutants on timescales between 1 ps and 10 ns using a versatile streak camera setup. The work will also resolve structure-function relationships of the FAD binding site during catalysis and at different states of reduction.

Here, we present time-resolved fluorescence spectra of the FAD cofactor in three structurally similar molybdo iron-sulfur flavoproteins, which are the [CuSMoO₂] CO dehydrogenase from *Oligotropha carboxidovorans*, the [MoSO₂] xanthine dehydrogenase from chicken liver and the [MoSO₂] xanthine oxidase from bovine milk.

MO 16.8 Di 14:00 Poster C1

Mid and Near-Infrared spectra of conformers of H-Pro-Trp-OH and H-Trp-Ser-OH — KAI SEEFELD¹, ●THOMAS HÄBER¹, GERNOT ENGLER¹, STEFAN GRIMME², and KARL KLEINERMANN¹ — ¹Institut für Physikalische Chemie, Heinrich-Heine Universität Düsseldorf, Universitätsstr. 1, 40225 Düsseldorf, Germany — ²Theoretische Organische Chemie, Organisch-Chemisches Institut der Universität Münster, Corrensstraße 40, 48149 Münster, Germany

We present near and mid infrared-UV double resonance spectra of the natural di-peptides Pro-Trp and Trp-Ser. In the case of Pro-Trp two conformers are present in the supersonic expansion: a stretched conformer with fully extended backbone and a folded conformer with an OH...OC_{pep} hydrogen bond. Both conformers are stabilized by dispersion interaction between indole ring and peptide backbone and a NH_{pep}/N_{proline} contact. Trp-Ser has two detectable conformers in supersonic expansions. The two conformers both have folded structures where both OH groups are involved in hydrogen bonds. The vibra-

tional and conformational assignment is supported by DFT and *ab initio* calculations. An adequate description of the energetic order of different conformers requires the explicit inclusion of dispersion. The lowest energy conformers in both systems have peptide backbones that lie on top of the indole ring.

MO 16.9 Di 14:00 Poster C1

Radiation damage studies on water-embedded biomolecules

— ●SADIA BARI¹, MAARTEN INKLAAR¹, DOMINIK GOSSET², FEMKE VAN SEIJEN¹, RONNIE HOEKSTRA¹, and THOMAS SCHLATHÖLTER¹ — ¹KVI Atomic Physics, University of Groningen, The Netherlands — ²ENSIAME, Valenciennes, France

The current increasing social and corporate interest in proton- and heavy ion-therapy of malignant tumors now results in the construction of first particle treatment centers. The chemical and biological aspects of biological radiation damage have been studied in great detail. However, little is known about biological radiation action on the molecular level and fs-timescales. First studies focused on gas phase DNA related molecules and neglected influences of the chemical environment.

To investigate these influences we built an electrospray ionization (ESI) source to form clusters from DNA molecules surrounded by water. Cooling and mass selection in a RF quadrupole ion trap ensures sufficient cluster density. After keV-ion irradiation collision products are extracted from the trap into a time-of-flight mass spectrometer.

MO 16.10 Di 14:00 Poster C1

The Interplay between Symmetry and Electronic Structure of Pigment-Protein Complexes from Purple Bacteria

— ●RALF KUNZ¹, MARTIN RICHTER¹, SILKE OELLERICH¹, JÜRGEN BAIER¹, THOMAS PREM¹, FRANCESCO FRANCA², GIOVANNI VENTUROLI², DIETER OESTERHELT³, JUNE SOUTHALL⁴, RICHARD COGDELL⁴ und JÜRGEN KÖHLER¹ — ¹Experimentalphysik IV, Universität Bayreuth — ²University of Bologna — ³MPI für Biochemie, Martinsried — ⁴University of Glasgow

A recent rather low resolution X-ray crystal structure of the RC-LH1 core complex from the photosynthetic purple bacterium *Rps. palustris* showed the presence of a physical gap in the LH1 ring. The presence of such a gap, though functionally critical for the cyclic electron transport in the photosynthetic process, has become very controversial. We have now applied single-molecule spectroscopy to the RC-LH1 complexes of the purple bacteria *Rps. palustris* and *Rb. sphaeroides* (*pufX*- strain) to demonstrate that there is such a gap in the LH1 ring structure. More than 80% of the complexes from *Rb. sphaeroides* only show broad absorption bands, whereas all of the measurable complexes from *Rps. palustris* also have a narrow line at the low-energy end of their spectrum. We describe how the presence of this narrow feature indicates the presence of a gap in the electronic structure of the LH1 from *Rps. palustris*, which provides strong support for the physical gap that was previously modelled in its X-ray crystal structure.

MO 16.11 Di 14:00 Poster C1

Fluorescence correlation spectroscopy on flavoproteins

— ●CHRISTIAN BROCK¹, FLORIAN SPREITLER², ASTRID PELZMANN³, ORTWIN MEYER⁴, and JÜRGEN KÖHLER⁵ — ¹Lehrstuhl für Experimentalphysik 4, Universität Bayreuth — ²Lehrstuhl für Experimentalphysik 4, Universität Bayreuth — ³Lehrstuhl für Mikrobiologie, Universität Bayreuth — ⁴Lehrstuhl für Mikrobiologie, Universität Bayreuth — ⁵Lehrstuhl für Experimentalphysik 4, Universität Bayreuth

We use fluorescence correlation spectroscopy to investigate the binding properties of CO-dehydrogenase, a flavoenzyme that plays an important role in the respiratory chain of the CO-oxidizing bacterium *Oligotropha carboxidovorans*. CO-dehydrogenase is labeled with fluorescein, and the change of its diffusion-coefficient upon binding to a lipid vesicle is monitored. This experiment will be repeated with modified versions of the enzyme, lacking certain functional groups that are supposed to be responsible for binding. Furthermore, triplet kinetics of FAD and riboflavin have been analyzed.

MO 17: Elektronische Spektroskopie

Zeit: Dienstag 14:00–19:00

Raum: Poster C1

MO 17.1 Di 14:00 Poster C1

High resolution Fourier transform spectroscopy on LiRb

— ●ALEXANDER STEIN¹, ASEN PASHOV², MILENA IVANOVA², HORST KNÖCKEL¹, and EBERHARD TIEMANN¹ — ¹Leibniz Universität Hannover, Welfengarten 1, 30167 Hannover — ²Department of Physics, Sofia University, 5 J. Bourchier blvd., 1164 Sofia, Bulgaria

The LiRb molecule is one of the few heteronuclear alkali metal molecules (along with those containing one Fr atom), for which accurate spectroscopic information is still missing. On the other hand it is one of the most polar among the alkali molecules and is surely of interest in experiments with mixtures of cold atoms (e.g. D. DeMille, Phys. Rev. Lett. 88, 067901 (2002)). We report the first high resolution observation of laser-induced fluorescence in the LiRb molecule. Abundant experimental information is collected with a typical resolution of 0.03 cm⁻¹ applying a Fourier-transform spectrometer. The present status of the analysis and preliminary potentials for the X¹Σ⁺ ground state and the two lowest ¹Π states are presented.

MO 17.2 Di 14:00 Poster C1

High resolution Fourier transform spectroscopy on Sr₂

— ●ALEXANDER STEIN, HORST KNÖCKEL, and EBERHARD TIEMANN — Leibniz Universität Hannover, Welfengarten 1, 30167 Hannover

Strontium actually is a candidate for a new and more precise frequency standard (e.g. I. Courtillot et al., Phys. Ref. A 68, 030501(R) (2003)). Hence there is a high interest in cooling and trapping of cold strontium atoms (M. Yasuda and H. Katori, Phys. Rev. Let. 92, 153004 (2004)). At the moment there are no sufficiently precise potentials available for the Sr₂ molecule allowing the calculation of collisional properties as the scattering length.

We report on new spectroscopic investigations using a heat pipe setup. The current status of the experiment and improved potentials of the X¹Σ_g⁺ ground state and the excited 2(A)¹Σ_u⁺ state will be presented.

MO 17.3 Di 14:00 Poster C1

Transient Spectroscopy of UV excited flavone and substituted porphyrins: Triplet-Triplet absorption and comparison with theory

— ●GERNOT ENGLER¹, DENNIS LÖWENICH¹, KARL KLEINERMANN¹, MARTIN KLEINSCHMIDT², CHRISTEL MARIAN², and SERGEJ KOVALENKO³ — ¹Institute for Physical Chemistry, Heinrich-Heine-University, Universitätsstr. 1, D-40225 Düsseldorf, Germany — ²Institute for Theoretical Chemistry, Heinrich-Heine-University, Universitätsstr. 1, D-40225 Düsseldorf, Germany — ³Institute for Chemistry, Humboldt University of Berlin, Brook-Taylor-Strasse 2, D-12489, Berlin, Germany

We reinvestigated the triplet absorption of flavone in solvents with different polarity at excitation wavelengths of 266 nm and 355 nm. Strong solvent dependent shifts of the transient absorption spectrum can be explained by comparison with TDDFT/MRCI calculations. We also investigated the triplet absorption of tetraphenylporphyrin (TPP), tetracarboxyphenylporphyrin (TCPP) and tetrahydroxyphenylporphyrin (THPP) in cyclohexane and ethanol in the spectral range 280-800 nm and observed T1-TN absorption at 320, 370, 440 and 470 nm which could be assigned to specific transitions by comparison with TDDFT/MRCI calculations. TCPP and THPP showed transient absorption at similar wavelengths and similar T1- lifetimes of a few us. The rise times both of the flavone and porphyrin transients are < 20 ns pointing to very efficient S1-T1 intersystem crossing.

MO 17.4 Di 14:00 Poster C1

Aufbau und Charakterisierung einer durchstimmbaren Kurzpuls Vakuu-UV Quelle für zeitaufgelöste Anregungs-Nachweis Experimente

— ●EGILL ANTONSSON, JÜRGEN PLENGE, ANDREAS WIRSING und ECKART RÜHL — Physikalische und Theoretische Chemie, Institut für Chemie und Biochemie, Freie Universität Berlin, Takustr. 3, 14195 Berlin

Es wird eine Kurzpuls Vakuu-UV Strahlungsquelle vorgestellt, die auf der Emission eines laserinduzierten Plasmas beruht und kontinuierlich durchstimmbare Vakuu-UV Strahlung im Photonenenergiebereich 10-30 eV liefert. Der Aufbau des Anregungs-Nachweis Ex-

periments beinhaltet ein Femtosekunden-Lasersystem (Pulsdauer: 85 fs; Pulsenergie: 30 mJ) zur Erzeugung des Plasmas auf der Oberfläche eines Wolfram-Drahtes, einen Vakuum-UV Monochromator zur Wellenlängeauswahl und ein Flugzeit-Massenspektrometer. Es werden Anregungs-Nachweis Experimente vorgestellt, in denen der $1s^2(^1S) \rightarrow 1s3p(^1P)$ Übergang von Helium bei 23,09 eV angeregt wird. Der angeregte $1s3p(^1P)$ Zustand wird nachfolgend mit Femtosekunden Laserpulsen ($\lambda = 402,5$ nm) ionisiert. Aus dem zeitabhängigen Anstieg des He^+ -Signals wird die Pulsdauer der VUV-Strahlung ermittelt, wobei eine Pulsdauer von 75 ± 20 ps erreicht wird. Mögliche Anwendungen der durchstimmbaren Kurzpuls Vakuum-UV-Quelle für zeitaufgelöste Anregungs-Nachweis Experimente werden diskutiert.

MO 17.5 Di 14:00 Poster C1

CH- π interactions in Benzene-Acetylene clusters — ●MATTHIAS BUSKER, THOMAS HÄBER, MICHAEL NISPEL, and KARL KLEINERMANN — Institut für Physikalische Chemie I, Heinrich Heine Universität Düsseldorf, Germany

CH- π interactions are interesting due to their importance for the stabilization of supramolecular aggregates, crystal packing, molecular recognition and folding of proteins. We present new gas phase results on medium-sized clusters of Benzene(B) with Acetylene(A) by using IR-UV double resonance spectroscopy for analysis. The investigated B_1A_{1-4} and B_2A_{1-2} aggregates were structurally assigned based on comparison of their infrared spectra with ab initio calculated frequencies and intensities and by taking the shift of their electronic spectra into account. The obtained cluster structures were compared with the basic structural units of BA 1:1 cocrystals obtained via x-ray analysis.

MO 17.6 Di 14:00 Poster C1

Manifestation of lifetime vibrational interference in the decay of resonantly excited $N^*O \pi^*(v)$ and $NO^* \pi^*(v)$ states into the $NO^+ A$ state — ●A. EHRESMANN¹, W. KIELICH¹, L. WERNER¹, P.V. DEMEKHIN², D.V. OMELYANENKO², V.L. SUKHORUKOV², K.-H. SCHATNER³, and H. SCHMORANZER⁴ — ¹Institute of Physics and CIN-SaT, University of Kassel, 34132 Kassel, Germany — ²Rostov State University of Transport Communications, 344038 Rostov-on-Don, Russia — ³I. Institute of Physics, Justus-Liebig University Giessen, 35392 Giessen, Germany — ⁴Department of Physics, Kaiserslautern University of Technology, 67653 Kaiserslautern, Germany

Dispersed fluorescence from the A-X(v') bands in the NO^+ ion produced after de-excitation of the $\pi^*(v)$ resonances of N^*O and NO^* has been measured in the spectral range of 118 nm - 142 nm. This fluorescence results from the participator Auger decay of the π^* resonances into the $NO^+ A$ state. Ab-initio calculations of the transition probabilities between vibrational levels of the resonant state were used to explain the observed intensity dependences for the A(v')-X(v'') fluorescence bands on the exciting-photon energy across the inner-shell resonances and on both v' and v'' vibrational quantum numbers. The multiplet structure of the π^* resonance and lifetime vibrational inter-

ference explain the observed exciting-photon energy dependence of the observed A-X fluorescence bands.

MO 17.7 Di 14:00 Poster C1

Isotope-specific and ultra-sensitive detection of nitric oxide: Application to exhaled air analysis — CHRISTOPH MITSCHERLING, ●CHRISTOF MAUL, and KARL-HEINZ GERICKE — Institut für Physikalische und Theoretische Chemie, Technische Universität Braunschweig, 38106 Braunschweig, Hans-Sommer-Str. 10

Laser-induced fluorescence (LIF) and resonance-enhanced multiphoton ionization (REMPI) are extremely sensitive spectroscopic techniques for the investigation of low nitric oxide (NO) concentrations.

The mass selectivity of the REMPI method allows to identify spectral windows in which the most abundant isotopologues $^{14}N^{16}O$, $^{15}N^{16}O$, and $^{14}N^{18}O$ can be monitored free from spectroscopic interference by each other. For this detection the $A^2\Sigma^+ \leftarrow X^2\Pi$ transition (NO γ bands) is used which is easily accessible in the ultraviolet wavelength range around 225 nm.

Carefully selected rovibrational transitions are employed for the isotope-specific, ultra-sensitive detection of NO in exhaled air by laser induced fluorescence. Applications to on-line NO measurements for human breath analysis will be presented and discussed.

MO 17.8 Di 14:00 Poster C1

Optical excitation and detection of nitrous oxide in the ultraviolet wavelength range — ●CHRISTOF MAUL — Institut für Physikalische und Theoretische Chemie, Technische Universität Braunschweig, 38106 Braunschweig, Hans-Sommer-Str. 10

N_2O is a widely used precursor molecule for $O(^1D)$ atoms, in particular for investigating the bimolecular reaction $O(^1D) + N_2O \rightarrow 2 NO$ which can be initiated with relative experimental ease by 193 nm laser radiation in a N_2O sample. More often than not, such experiments are performed in supersonic expansions where low temperature and high number density favour the formation of N_2O clusters which might affect the course of the reaction. Therefore, a method for characterization of the N_2O sample under the conditions of a reactive scattering experiment is desirable.

State selective excitation and detection of N_2O through its Rydberg states is possible by resonance enhanced multi-photon ionization (REMPI) spectroscopy. Only two such studies have been published up to date, mainly relying on a (3+1)-REMPI scheme in the wavelength range from 350 nm to 370 nm. Data on (2+1)-REMPI excitation are less abundant and exist only for selected wavelength ranges and temperatures. Cluster formation has neither been investigated nor investigated.

The aim of the presented work is to characterize (2+1)-REMPI spectroscopy of N_2O in the wavelength range from 235 nm to 245 nm under different experimental conditions, i.e. for room temperature and jet-cooled samples, and to explore the possibility of cluster detection.

MO 18: Femtosekundenspektroskopie

Zeit: Dienstag 14:00–19:00

Raum: Poster C1

MO 18.1 Di 14:00 Poster C1

Femtosecond Optical and Vibrational Spectroscopy of Flavins and Flavoproteins — ●ALEXANDER WEIGEL and LUIS PEREZ LUSTRES — Institute for Chemistry, Brook-Taylor-Str. 2, 12489 Berlin

Flavin photoreceptors form a newly discovered class of blue-light sensing proteins which bind flavin chromophores as cofactors. Excitation of the chromophore leads to long living conformational changes in the protein, which trigger multiple biological responses. Contrary to the other known photoreceptor families, photactivation of flavoproteins does not occur by E/Z isomerization but displays unusual activation mechanisms which remain largely unknown. We apply femtosecond broadband transient absorption and report here on riboflavin and the phototropin mutant LOV1C57S. In the latter a critical cysteine residue was substituted by serine to hinder signalling state formation. Ultrafast loss of oscillator strength in riboflavin on a ~ 10 fs timescale is assigned to vibronic coupling between the optically active $\pi\pi^*$ state and the dark $\pi\pi^*$ state. In the LOV1 mutant we were able to resolve spectral hole-burning at early time and its development on a 100 fs time scale. Weak spectral evolution with 1 ps time constant reflects struc-

tural reorganisation of the cofactor in the protein pocket. Vibrational wavepackets give rise to strong oscillations with frequencies ranging from 40 to 500 cm^{-1} . Remarkably, a 190 ps time constant and a series of oscillations with zero phase over the 20,000 cm^{-1} spectral window exhibit similar spectral amplitudes, which may reflect coherent oscillations from vibronic coupling in the mutant. We present first results from broadband femtosecond stimulated Raman spectroscopy.

MO 18.2 Di 14:00 Poster C1

Controlling the photodissociation dynamics of methyl iodide — A. KLUMPP¹, M. KRUG¹, ●C. LUX¹, M. WOLLENHAUPT¹, J. DURA², J.G. IZQUIERDO², R. DE NALDA², L. BANARES², and T. BAUMERT¹ — ¹Universität Kassel, Institut für Physik und — ²Universidad de Complutense Facultad de Ciencias Químicas

Due to its simple structure but nevertheless complex and interesting dissociation dynamics methyl iodide is a well investigated molecule in femtochemistry (e.g. [1, 2]). In previous fs experiments (e.g. [2]) the methyl iodide bond was broken and the methyl was probed with REMPI radiation. In our experiment, we used a shaped femtosecond

800 nm pulse [3] in addition to exert control during the pump probe sequence. Pulse shaping was performed in the frequency domain applying polynomial spectral phases. The methyl states ($^3Q_0, ^1Q_1 \nu = 0, ^1Q_1 \nu = 1$) [4] were detected using a velocity-map-imaging method [5]. Using the pulse shaper in combination with an evolutionary algorithm the ratio of the ion yield corresponding to molecular states was optimized. The yields of the above photo-products were studied as a function of the relative pulse delay and chirp parameter in a two dimensional map.

- [1] D. Zhong and A.H. Zewail, *J.Phys.Chem.A* 102, 4031 (1998)
- [2] R. de Nalda, et al., *J.Chem.Phys.* 126, 021101 (2007)
- [3] A. Präkelt et al., *Rev.Sci.Instr.*, 74, 11, 4950 (2003)
- [4] Y. Amatatsu, et al., *J. Chem. Phys.* 104, 9783 (1996)
- [5] A.T.J.B. Eppink et al., *Rev.Sci.Instrum.* 68, 3477 (1997)

MO 18.3 Di 14:00 Poster C1

Influence of environment on rotational wave packets in gases — ●JOCHEN MAURER, NINA OWSCHMIKOW, FALK KÖNIGSMANN, and NIKOLAUS SCHWENTNER — Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin

A linearly polarized short laser pulse interacts with a molecule with anisotropic polarizability via non-resonant Raman transitions and induces recurrent transient alignment of the molecular axis along its electric field direction. This rotational wave packet leads to a time-dependent change in birefringence of the sample which we detect using optical Kerr effect spectroscopy (OKE). We use a Ti:Sa laser (wavelength 780 nm, pulse length 150 fs) that is focused to an intensity of up to 10^{14} W/cm² to create alignment of N₂ molecules in the gas phase. Our experiments cover pressures ranging from few mbar to 5 bar and temperatures from 80 K to 300 K. We find a quadratic increase in signal intensity with density characteristic for coherent superpositions. In addition to this effect the signal amplitude grows in accordance with theoretical predictions on the susceptibility $\chi^{(2)}$, as with decreasing temperature the thermal occupation of rotational levels is narrowed. The homodyne detected signal is proportional to the square of the degree of alignment $\langle \cos(\theta)^2 \rangle^2$ and decays with time as the wave packet dephases due to bimolecular collisions. We study the temporal evolution of the degree of alignment depending on pressure in pure N₂ and mixtures of N₂ with the noble gases He, Ar and Kr. From the rate of decay of revivals we extract interaction radii for dephasing and find that dephasing is mainly due to inelastic collisions.

MO 18.4 Di 14:00 Poster C1

Zur kohärenten Kontrolle matrixinduzierter Prädissoziation von Brommolekülen in einer festen Argon Umgebung — ●LISA-MARIE KROCKER¹, MÓNICA HÉJAS¹, HEIDE IBRAHIM¹, MARKUS GÜHR² und NIKOLAUS SCHWENTNER¹ — ¹Freie Universität Berlin, Institut für Experimentalphysik, Arnimallee 14, 14195 Berlin — ²Stanford PULSE Center, Varian Physics Bldg., 382 Via Pueblo Mall, Stanford CA 94305-4060, USA

Neue Resultate frequenz aufgelöster Spektroskopie an Brom in einer Argon-Matrix zeigen eine effiziente Prädissoziation auf einer Pikosekunden-Zeitskala [1]. Die schnelle Zeitentwicklung dieser chemischen Reaktion wird von uns mittels Femtosekunden-Pump-Probe-Spektroskopie verfolgt. Dies geschieht durch simultane Beobachtung der molekularen Schwingungswellenpaketdynamik auf den verschiedenen elektronischen Potentialen zwischen denen der Populationstransfer stattfindet. Durch Vergleich mit der Dynamik auf den einzelnen Potentialen und durch Polarisationsanalyse lassen sich die prädissoziativen Wellenpaketanteile im ursprünglich angeregten B-Zustand in Form eines Signalabfalls (etwa 10% pro Umlauf) identifizieren. Nach der Dissoziation über den repulsiven Zustand werden diese Anteile durch den Käfigeffekt der Matrix wieder in einen gebundenen Bereich des A-Zustandes überführt und dort als entsprechender Signalanstieg nachgewiesen. Weiterhin zeigen wir, wie sich mithilfe geeignet geformter Anregungspulse die Effizienz der Prädissoziation modifizieren lässt. [1] H. Ibrahim, M. Gühr und N. Schwentner, *J. Chem.Phys.* 2007, akzeptiert

MO 18.5 Di 14:00 Poster C1

Anisotropy in ultrafast experiments — ●ANDREAS-NEIL UNTERREINER and OLIVER SCHALK — Universität Karlsruhe (TH), Lehrstuhl für Molekulare Physikalische Chemie, 76128 Karlsruhe

A new ansatz for anisotropy in ultrafast experiments is presented. It is capable of describing systems with non-degenerate, degenerate and quasi-degenerate excited states (the latter concerning systems which are excited near a conical intersection) for one- or multiphoton pump-

probe experiments. This contribution focuses on degeneracy and quasi-degeneracy. The degenerate case exhibits a high time zero anisotropy that decays due to coherence and population decay. This decay can be described with an Ornstein-Uhlenbeck process. Discrepancies to former models are discussed. In this model, quasi-degeneration in anisotropy experiments can be explained as a mixture of non-degenerate and twofold degenerate excited states and represents the first quantitative description of such processes.

MO 18.6 Di 14:00 Poster C1

Long living, coherent phonons in quantum-crystals: cryogenic normal- and para-hydrogen — ●FALK KÖNIGSMANN¹, DAVID T. ANDERSON², and NIKOLAUS SCHWENTNER¹ — ¹Freie Universität Berlin, Institut für Experimentalphysik, Arnimallee 14, D-14195 Berlin — ²Department of Chemistry, University of Wyoming, Laramie, WY 82071, USA

Coherent optical phonons are a hot topic in metals and insulators, but did not show up in previous ultrashort pulsed excitations of quantum crystals. We grow 3 cm long, transparent para- and normal-hydrogen crystals in an enclosed cell at 8 K, which are then cooled down to 4 K. The crystals are pumped with 150 fs pulses at 780 nm of a Ti:Sa amplified laser system and the induced birefringence is detected with the second harmonic in a colinear way. We observe long lasting (> 20 ps) sinusoidal birefringence modulation with a period of 900 fs in para-hydrogen. While the phonon density of states would cover a broad range from 0-180 wavenumbers, the observed coherent phonon has a sharp frequency centered at 36,8 wavenumbers. It coincides with the transverse, optical phonon at the center of the Brillouin-zone, which is observed exclusively in Raman scattering. The phonon wave packet is anisotropic and the amplitude lies perpendicular to the c axis. In normal-hydrogen the same class of phonon, slightly shifted to higher frequencies and more strongly dampened, is observed.

MO 18.7 Di 14:00 Poster C1

High Harmonic Generation on Molecular Excited Electronic States — ●MARKUS GÜHR, BRIAN K. MCFARLAND, JOE P. FARRELL, and PHILIP H. BUCKSBAUM — Stanford PULSE Center, Stanford University and SLAC, California, USA

We discuss schemes for the generation of high harmonics on excited electronic states of molecules. The high harmonic generating pulse is used to probe the dynamics initiated with a first pump pulse. This opens the chance to observe dynamics on those states without involving other electronic states in a probe process.

The main difficulty arising is the low ionization potential and thus the inherent high ionization rate for molecules in the excited state. We present a method to overcome this problem using the symmetry of the molecular wave function.

A further complication is given by the fact that a small harmonic signal from the excited state is sitting on a big background from molecules in their electronic ground state. Four-wave-mixing techniques can be applied to generate a background-free signal. We present prototypical four-wave-mixing measurements, using the third harmonic generated in air.

MO 18.8 Di 14:00 Poster C1

Quantum dynamical simulations of femtosecond Pump-DFWM spectroscopy of higher excited states — ●JÖRG LIEBERS, ABRAHAM SCARIA, VINU NAMBOODIRI, JAKOW KONRADI, ARNULF MATERNY, and ULRICH KLEINEKATHÖFER — Jacobs University Bremen, Germany

Nonlinear time- and frequency-resolved four-wave mixing (FWM) spectroscopy is one of the major tools to investigate dynamic properties of molecules. Until now the dynamics of the ground state and lower lying excited states were accurately investigated in numerous experiments. Recently it was demonstrated that dynamics of higher lying excited states in molecular iodine can be accessed and probed by a time-resolved DFWM process as well by combining the DFWM process with an initial pump pulse [1]. In this contribution we present the results of quantum dynamical simulations of rovibrational wavepackets which reproduce the results of these experiments. The wavepacket dynamics on the potential energy surfaces of the ion pair states of iodine were calculated for different pulse sequences and compared to the dynamics monitored in the experiments. The experiments are detailed in a separate contribution.

[1] A. Scaria, V. Namboodiri, J. Konradi, and A. Materny, *J. Chem. Phys.* 127, 144305 (2007)

MO 18.9 Di 14:00 Poster C1

Detection of C-Deuterium compounds by CARS microscopy — ●GERO BERGNER^{1,3}, DENIS AKIMOV¹, MICHAEL SCHMITT^{1,2}, SEBASTIAN SCHLÜCKER³, and JÜRGEN POPP^{1,2} — ¹Institut für Photonische Technologien, Albert-Einstein-Straße 9, 07745 Jena — ²Institut für Physikalische Chemie, Lessingstraße 10, 07743 Jena — ³Institut für Physikalische Chemie, Am Hubland, 97074 Würzburg

Coherent anti-Stokes Raman scattering (CARS) microscopy is a powerful imaging technique with chemical specificity. In particular, it provides vibrational contrast without need of external labelling. Here, we present first steps to establish CARS as a new method for drug localization in living cells. Chemical contrast in the images is obtained by probing the C-D stretch vibration of internally labelled (Deuterium-substituted) compounds. For determining the ratio of Raman-resonant signal to non-Raman-resonant background, both C-D and C-H species of the same compound are investigated. First results for systematically determining the detection limit of this methodology are presented.

MO 18.10 Di 14:00 Poster C1

A Comparison of the Selective Excitation of Molecular Modes in Gas and Liquid Phase Using Femtosecond Pulse Shaping — ●ABRAHAM SCARIA, VINU NAMBOODIRI, JAKOW KONRADI, and ARNULF MATERNY — Jacobs University Bremen, Germany

In our previous publications we have demonstrated that a selective excitation of specific vibrational modes in a molecule is possible by using a feedback-controlled optimization in a coherent-anti Stokes Raman scattering (CARS) process [1,2]. The mechanism behind the selective enhancement and suppression of vibrational modes is not clearly understood. The experiments suggest an important contribution by intermolecular dynamical processes. Here, it would be of importance to determine, what influence the interaction with surrounding molecules plays on the control result. In our contribution, we present results from optimal control experiments performed on CS₂ molecules in the gas phase as well as in its liquid form. The CARS excitation was chosen to be not in resonance with an electronic transition in the molecule but to excite different vibrational modes coherently. A pure phase modulation of the Stokes pulse resulted in changes of the ratio of the Raman lines observed in the nonlinear scattering spectrum. This could also be achieved when no temporal shift between pump and Stokes laser resulted in a simple change of the Raman resonances. The differences between gas and liquid phase measurements will be discussed.

[1] J. Konradi, A.K. Singh, and A. Materny, *PCCP* **7**, 3574 (2005).

[2] J. Konradi, A. Scaria, V. Namboodiri, and A. Materny. *J. Raman Spectrosc.* **38**, 1006 (2007).

MO 18.11 Di 14:00 Poster C1

Ultrakurze Laserimpulse zur Anregung von Photosensibilisatoren — ●JOHANNES SCHNEIDER, JUTTA MILDNER, MATTHIAS WOL-

LENHAUPT und THOMAS BAUMERT — Universität Kassel, Institut für Physik und CINSaT, Heinrich-Plett-Str. 40, D-34132 Kassel

Photosensibilisatoren werden typischer Weise mit kontinuierlichem Licht angeregt. Nach dem Übergang aus einem angeregten Singulett-Zustand ins Triplett-System (ISC) wird die Anregungsenergie dieser Systeme mittels Energietransfer effizient an Moleküle der Umgebung abgegeben.

Bei Anregung mit Femtosekunden-Laserimpulsen kann die Dynamik der Anregung mit hoher Zeitauflösung untersucht werden. Zudem erhält man mittels Impulsformung die Möglichkeit den Anregungsprozess des Moleküls zu beeinflussen.

Als Beobachtungsgrößen für unsere Experimente dienen Absorption, Fluoreszenz und Phosphoreszenz der Photosensibilisatoren in der flüssigen Phase. Besonderes Augenmerk gilt dem ISC-Prozess, welcher die Effizienz der Photosensibilisierung einschränkt. Der direkte Nachweis dieses Übergangs gelingt über die Phosphoreszenz von gelöstem Sauerstoff nach erfolgtem Energietransfer vom Photosensibilisator. Dieses Signal steht am Ende der Reaktion und eignet sich damit für eine rückkopplungsgesteuerte Optimierung.

Der Aufbau zur Messung der Lumineszenzen und zur Aufnahme von Absorptionstransienten wird präsentiert. Erste Untersuchungen an Zink-Porphyrin und Porphyrzinen werden vorgestellt.

MO 18.12 Di 14:00 Poster C1

Phase modulation of ultrashort laser pulses by rotational wave packets — ●RAPHAEL KUHNEN and BERND V. ISSEENDORFF — Universität Freiburg, physikalisches Institut, Stefan-Meier-Strasse 19, D-79104 Freiburg

Molecular rotational wave packets introduce a time dependent phase modulation to ultrashort optical pulses. This phase modulation can be imaged by observing the spectrum of a probe laser pulse sent with a tunable delay to an alignment pulse.

The processes affecting the probe laser pulse depend on the polarisation of the pump pulse. This influence as well as the temporal evolution of the rotational wave packets can be observed by recording the transmitted spectrum of a 400nm, linear polarized, laser pulse depending on the pump-probe delay as well as the rotation angle of a quarter-wave-plate in the pump-beam.

It is possible to tune the phase in a way that the spectrum of the laser pulse is broadened and shifted by raman scattering. As a result it is possible to introduce a negative chirp to the probe laser pulse and to reduce the pulse duration below 25 fs.

(1) M. Wittmann et al., *Appl. Phys. B*, **70**, 261 (2000)

(2) R.A. Bartels et al., *Phys. Rev. Lett.*, **88**, 1 (2002)

(3) V.P. Kalosha and J. Herrmann, *Phys. Rev. A*, **68** (2003)

(4) R. Torres et al., *Phys. Rev. A*, **72**, 023420 (2005)

MO 19: Photochemie

Zeit: Donnerstag 16:30–19:00

Raum: Poster C1

MO 19.1 Do 16:30 Poster C1

3D Velocity Mapping: Dynamics of the reaction O(¹D) + N₂O → 2NO photoinitiated in the (N₂O)₂ dimer — NIELS GOEDECKE¹, SEBASTIAN KAUCZOK¹, ●CHRISTOF MAUL¹, ALEXEY CHICHININ^{1,2}, and KARL-HEINZ GERICKE¹ — ¹Institut für Physikalische und Theoretische Chemie, TU Braunschweig — ²Institute of Chemical Kinetics and Combustion, Russian Academy of Sciences, Novosibirsk

3D velocity mapping allows state specific characterization of full three dimensional velocity distributions of reaction products following resonance-enhanced multi-photon ionization (REMPI). 3D resolution is achieved by using a time-of-flight (TOF) spectrometer equipped with a two-dimensional delay line behind a micro channel plate stack

which simultaneously returns impact position and time of the selected reaction product. Inserting an Einzel lens into the TOF spectrometer allows to map the product velocity and to get rid of image distortion due to the unavoidable length of the ionization laser focus.

The technique has been used to investigate the reaction of O(¹D) with N₂O in the (N₂O)₂ dimer. O(¹D) is generated by photodissociation of N₂O using an ArF excimer laser. The reaction yields two NO molecules which are subsequently ionized via a (1+1)-REMPI process by a dye laser. We have measured selected quantum state specific 3D velocity distributions of the NO product as well as spectra for several vibrational states ($v \leq 7$) of the electronic ground state X(²Π_g). The rotational temperature is low, in agreement with earlier investigations of the cluster reaction, but in striking contrast to the free collision.

MO 20: Quantenkontrolle

Zeit: Donnerstag 16:30–19:00

Raum: Poster C1

MO 20.1 Do 16:30 Poster C1

Control of nuclear spin selective rotation of methyl groups and symmetry adapted quantum dynamics — ●THOMAS GROHMANN and MONIKA LEIBSCHER — Freie Universität Berlin, Institut für Chemie und Biochemie, Takustr. 3, 14195 Berlin

The control of chemical reaction dynamics is currently intensively studied. However, the influence of the nuclear spin is only little investigated although nuclear spin isomers show different behaviour in their nuclear dynamics [1]. It has been shown, that time-dependent magnetic fields induce molecular rotations in methyl groups [2]. Our aim is to simulate the control of molecular torsion in methyl groups in order to create a molecular motor. Nuclear wavefunctions for methyl groups, obeying the anti-symmetry principle, can be constructed using molecular symmetry groups [3]. We derive the symmetry adapted wavefunctions for explicit model potentials describing nuclear torsion and vibration. By solving the time-dependent Schrödinger equation for the three protons in a time-dependent magnetic field we can show that it is only possible to induce unidirectional rotations if dipolar interactions between the nuclear spins are taken into account.

[1] O. Deeb, M. Leibscher, J. Manz, W. von Mueller and T. Seideman, *Chem. Phys. Chem.* **8** (2007), 322; T. Grohmann, O. Deeb, and M. Leibscher, *Chem. Phys.* **338** (2007), 252. [2] S. Clough, A.J. Horsewill, M.R. Johnson, J.H. Sutcliffe and I.B.I. Tomsah, *Europhys. Lett.* **29** (1995), 169. [3] S. Clough and P.J. McDonald, *J. Phys. C* **16** (1983), 5753.; K.W.H. Stevens, *J. Phys. C* **16** (1983), 5765.; D. Haase, private communication

MO 20.2 Do 16:30 Poster C1

Local control theory applied to molecular photoassociation — ●PHILIPP MARQUETAND and VOLKER ENGEL — Institut für Physikalische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

Local control theory (LCT) is employed to achieve molecular photoassociation with shaped laser pulses. Within LCT, the control fields are constructed from the response of the system to the perturbation which makes them accessible to a straightforward interpretation. This is shown regarding the ground-state collision of H+F atoms. The objective is to form vibrationally cold associated molecules. Results are presented for s-wave scattering, where the rotational degree of freedom is ignored and also for full scale calculations including rotations, in order to describe more realistic conditions.

MO 20.3 Do 16:30 Poster C1

A New Approach To Optimal Control Theory — ●CHRISTIAN

SCHWENKE¹, RONNIE KOSLOFF² und CHRISTIANE P. KOCH¹ — ¹Institut für Theoretische Physik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin — ²Department of Physical Chemistry, Hebrew University, Jerusalem 91904, Israel

Optimal control theory (OCT) was developed to find shaped pulses to control molecular dynamics. Switching the pulse on and off constrains the pulse in time and to create shaped pulses with fs lasers restricts spectral bandwidth. In the iterative approach [1] only one constraint, either in time or in frequency domain, can be imposed. We suggest an optimization scheme which allows for taking into account both constraints by combining the (t,t')-method [2] with OCT. The optimized fields will be found by solving a SCF-like problem.

[1] W. Zhu, J. Botina, H. Rabitz, *Rapid convergent iterative methods for quantum optimal control of population* *J. Chem. Phys.* **108**, 1953 (1998).

[2] U. Peskin, N. Moiseyev, *The solution of the time-dependent Schrödinger equation by the (t,t')-method: Theory, computational algorithm and applications* *J. Chem. Phys.* **99**, 4590 (1993).

MO 20.4 Do 16:30 Poster C1

Experimentelle Realisierung von Laserpulsen im von Neumann Phasenraum — ●ALEXANDER RODENBERG¹, SUSANNE FECHNER², FRANK DIMLER^{1,2}, TOBIAS BRIKNER^{1,2}, DAVID J. TANNOR³ und GUSTAV GERBER² — ¹Institut für Physikalische Chemie, Universität Würzburg, Am Hubland, 97070 Würzburg — ²Physikalisches Institut, Universität Würzburg, Am Hubland, 97070 Würzburg — ³Department of Chemical Physics, Weizmann Institute of Science, 76100 Rehovot, Israel

Im Gegensatz zur üblichen Darstellung des elektrischen Feldes im Frequenz- oder im Zeitraum bieten Phasenraumdarstellungen die Möglichkeit, die spektralen und zeitlichen Eigenschaften ultrakurzer Laserpulse simultan und auf intuitive Weise zu erfassen. Vor kurzem haben wir die von Neumann-Repräsentation eingeführt, die im Gegensatz zu den üblicherweise verwendeten eine vollständige Rekonstruktion des elektrischen Feldes bei gleichzeitigem Erhalt der intuitiven Interpretierbarkeit erlaubt. Sie ermöglicht, jeden Laserpuls aus elementaren Subpulsen aufzubauen.

Wir zeigen, wie diese von Neumann-Pulse durch spektrale Amplituden- und Phasenformung experimentell realisiert werden können und diskutieren die hierbei zu beachtenden experimentellen Randbedingungen. Mögliche Anwendungen in der Quantenkontrolle, wie die Vermessung von Fitnesslandschaften oder die Verbesserung vorhandener Lernalgorithmen, werden vorgeschlagen.

MO 21: Stossprozesse, Energietransfer

Zeit: Donnerstag 16:30–19:00

Raum: Poster C1

MO 21.1 Do 16:30 Poster C1

Electron impact ionisation of water molecules — ●ARNE SENTLEBEN, XUEGUANG REN, ALEXANDER DORN, and JOACHIM ULLRICH — Max-Planck-Institut für Kernphysik, 69117 Heidelberg

The single ionisation of water molecules by 95 eV electrons has been studied in a kinematically complete experiment. By employing a seeded supersonic beam vibrationally and rotationally cold H₂O molecules were accessible in the gas phase. The distributions of momenta for electrons and ions after the ionisation were measured using the reaction microscope technique. For non-dissociative ionisation of water fully differential cross-sections (FDCS) could be obtained. Additionally the dissociative ionisation channel leading to OH⁺ and H was investigated. Dependencies of the cross sections on the emission angle of the OH⁺ ions were found.

MO 21.2 Do 16:30 Poster C1

Electron-Exchange Parameter Measurements For Molecular Open-Shell-Targets — ●INGO HOLTKÖTTER and G. FRIEDRICH HANNE — Physikalisches Institut, 48149 Münster, Germany

Electron collisions with simple open-shell molecules such as O₂, NO or

NO₂ are important processes in both atmospheric physics and plasma chemistry. In our experiment, exchange collisions are observed directly by measuring the change of spin polarization after scattering of polarized electrons from unpolarized molecules with energies between 8 and 20 eV and scattering angles up to 130°. Since previous experimental results and theoretical calculations with O₂ and NO as target were not in satisfactory agreement, we revived these measurements to gain deeper insight into spin-exchange effects with open shell-molecules. For NO₂, we present the first experimental results for differential elastic electron exchange scattering at low energies.

With our recent measurements, we get a detailed view of the discrepancies between the experimental and older theoretical results. New calculations for electron exchange processes with O₂ as target show a very good agreement with our data. In other cases, however, there are still discrepancies between the experimental results and theoretical calculations.

At the conference, we will present our data for the electron exchange parameter for elastic scattering of spin-polarized electrons with O₂, NO or NO₂ at energies between 8 and 20 eV and compare them to available theoretical models.

MO 21.3 Do 16:30 Poster C1

Dissoziativer Zweifachelektroneneinfang in Ar⁸⁺ und H₂ Stoßprozessen — ●DOROTA HANT, NADINE NEUMANN, LOTHAR SCHMIDT, JASMIN TITZE, MARKUS SCHÖFFLER, OTTMAR JAGUTZKI, HORST SCHMIDT-BÖCKING und REINHARD DÖRNER — Institut für Kernphysik, Universität Frankfurt, Deutschland

Um dynamische Korrelationen in Atomen und Molekülen beschreiben zu können, ist ein genaues Wissen aller inneren Freiheitsgrade des Grundzustands erforderlich. Mit Hilfe der Quantenmechanik kann der Grundzustand eines atomaren oder molekularen Systems berechnet werden. Eine genaue Messung dieses Grundzustands ist jedoch mit experimentellen Methoden nicht möglich. Die Entwicklung eines geeigneten experimentellen Aufbaus sollte die Messung aller externen Freiheitsgrade und dadurch einen Rückschluss auf den Grundzustand ermöglichen. Bei dem hier vorgestellten Experiment gilt ein besonderes Augenmerk dem Zweifachelektroneneinfang, welcher bei der Reaktion von Ar⁸⁺ auf molekularen Wasserstoff untersucht werden soll. Die langsamen, hochgeladenen Projektionen werden aus der Elektron-Zyklotron-Rezonanz (EZR) Ionenquelle am Institut für Kernphysik in Frankfurt mit jeweils 5 und 15 keV/u beschleunigt und in der Reaktionszone mit einem Überschallgasjet gekreuzt. Der Nachweis der Wasserstoffionen erfolgt dann mit Hilfe der Impulsspektroskopie (COLTRIMS). Ziel des Experiments ist der Vergleich zwischen dem schnellen, direkten und dem langsamen Verlauf (over-barrier Modell) des Zwifachelektroneneinfangs.

MO 21.4 Do 16:30 Poster C1

Dissociative electron capture in collisions between Ar⁸⁺ and CO₂ — ●NADINE NEUMANN, DOROTA HANT, LOTHAR PH. H. SCHMIDT, JASMIN TITZE, MARKUS SCHÖFFLER, ACHIM CZASCH, OTTMAR JAGUTZKI, HORST SCHMIDT-BÖCKING, and REINHARD DÖRNER — Institut für Kernphysik, J.W. Goethe Universität Frankfurt, Max-von-Laue Str. 1, D-60438 Frankfurt

We are using the Cold Target Recoil Ion Spectroscopy (COLTRIMS) to investigate the break up of CO₂ molecules in impact processes with slow highly charged ions. While the slow highly charged ions passes the CO₂ molecule electron capture into the projectile causes a conformation change of the CO₂ molecule. With the COLTRIMS set up we are able to measure the 4π solid angle in momentum space of the dissociating ion fragments. The motivation for this experiment is to ascertain the change of the CO₂ molecule conformation.

MO 21.5 Do 16:30 Poster C1

Dissoziation von dreiatomigem Wasserstoff — ●FRANK BAUMGARTNER, MICHAEL GISI und HANSPETER HELM — Universität Freiburg

Das neutrale dreiatomige Wasserstoffmolekül wurde in den letzten Jahren zum Gegenstand zahlreicher theoretischer und experimenteller Studien [1,2]. Besonderes Interesse kommt dabei dem Dreiteilchenzerfall in die Fragmente H(1s)+H(1s)+H(1s) zu, welcher direkten Einblick in die molekulare Dynamik nicht-adiabatischer Prozesse erlaubt. Dazu werden die Impulsvektoren aller entstehenden Dissoziationsfragmente

mit Hilfe einer Dreifach-Koinzidenz-Technik erfasst. Durch eine Modernisierung der Elektronik konnte die Ortsauflösung des bestehenden Detektors verdoppelt und die Zeitauflösung um einen Faktor drei gesteigert werden. Zugleich wurde das Datenaufnahmesystem stark verbessert und ermöglicht nun eine komplette Datenauswertung schon während der Messung.

Wir stellen erste experimentelle Ergebnisse vor, die den Dreiteilchenzerfall hochangeregter Rydbergzustände des H₃ zeigen. Es deutet sich an, dass dabei vorwiegend lineare Zerfallsgeometrien auftreten. Diese Beobachtung steht in Übereinstimmung mit Untersuchungen zur dissoziativen Rekombination von H₃⁺ Ionen [3] nach dem Einfang langsamer Elektronen.

- [1] U. Galster, M. Jungen, Phys. Rev. A **72** 062506 (2005)
- [2] R. E. Continetti et. al, Phys. Rev. Lett. **93** 153202 (2004)
- [3] D. Zajfman et. al, Phys. Rev. A **66** 032719 (2002)

MO 21.6 Do 16:30 Poster C1

Elektronentransfer in ausgerichtete Wasserstoff-Molekülonen bei langsamen Stößen mit Helium — ●SVEN SCHÖSSLER, LOTHAR PH. H. SCHMIDT, LUTZ FOUCHAR, HORST SCHMIDT-BÖCKING und REINHARD DÖRNER — Institut für Kernphysik der J.W.Goethe Universität, Max-von-Laue-Str. 1, 60438 Frankfurt am Main, Deutschland

Bei Stoßgeschwindigkeiten unter 1 a.u. wurde der dissoziative Elektronentransfer bei der Reaktion H₂⁺ + He → H₂* + He⁺ → H + H + He⁺ untersucht. Das He⁺ Rückstoßion wurde mit der COLTRIMS-Methode vermessen und koinzident dazu die beiden neutralen Wasserstoff-Atome des Projektils auf einem ortsauflösenden multihitfähigen MCP-Detektor mit Delay-Line-Auslese detektiert.

Die kinematisch vollständige Messung erlaubt die Selektion des Reaktionskanals, bei dem sowohl die Molekülfragmente als auch das He⁺ Target im elektronischen Grundzustand sind. Für diesen Kanal werden die Daten in inverser Kinematik (ein He-Atom streut an einem H₂⁺ Molekül) präsentiert. Aus der Aufbruchrichtung des Moleküls kann die Orientierung beim Stoß bestimmt werden. Für die Reaktionen, bei denen das Molekül senkrecht zur Strahlrichtung gestanden hat, wird für das He-Ion ein Beugungsmuster beobachtet, das mit guter Näherung als Interferenz von zwei Kugelwellen beschrieben werden kann.

MO 21.7 Do 16:30 Poster C1

Nonadiabatic molecular dynamics simulations of C₆₀-C₆₀ collisions — ●JAN HANDT and RÜDIGER SCHMIDT — Institut für Theoretische Physik, Technische Universität Dresden, D-01062 Dresden

We present a theoretical study of the high-energy collision dynamics as well as of the low-energy collision dynamics influenced by laser irradiation. In both the cases electronic excitation has to be considered, i.e. a nonadiabatic approach is necessary. Using a combination of molecular dynamics and time-dependent density functional theory we can describe the nonadiabatic dynamics. We show computational results of collisions up to energies of 1 MeV where electronic excitation dominates, and effects of the laser light for fusion processes in the low-energy range.

MO 22: Theorie: Quantenchemie und Moleküldynamik

Zeit: Donnerstag 16:30–19:00

Raum: Poster C1

MO 22.1 Do 16:30 Poster C1

Approaches to Time-Dependent Multicomponent Dynamics — ●CHIRAG JHALA and MANFRED LEIN — Institute of Physics, Universität Kassel, Heinrich-Plett-Str. 40, 34132 Kassel, Germany.

Multicomponent density functional theory (MCDFT) for molecules treats electrons and nuclei on the same footing. Since practical functionals for time-dependent MCDFT are hardly available, we consider an H₂⁺ model system, where we can calculate the exact Kohn-Sham (KS) potentials by solving the time-dependent Schrödinger equation and inverting the time-dependent KS equations. As an alternative approach to MCDFT, we propose to use the stationary action principle in combination with an explicitly correlated ansatz for the full time-dependent wave function. By using an ansatz with orbitals depending on transformed coordinates, it is hoped that one needs less configurations than in the standard multi-configuration time-dependent Hartree method for accurate results.

MO 22.2 Do 16:30 Poster C1

Damping of vibrational dynamics in dimers attached to He nanodroplets — ●MARTIN SCHLESINGER and WALTER STRUNZ — Theoretische Quantendynamik, Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg

Femtosecond pump-probe spectroscopy is a well-established tool for studying vibrations in diatomic molecules [1]. Recent experiments investigate the evolution of vibrational wave packets excited in K₂ dimers attached to superfluid helium nanodroplets [2]. Deviations from gas-phase spectra are seen both in the time- and frequency domain. We simulate the pump-probe signal for the free molecule [3] and include different models to account for a possible damping of the wave packet due to the helium environment. For different damping constants, the effect is investigated by comparing with simulated gas-phase (no damping) and experimental spectra, for which we find good agreement. Our calculations show a shift of the central frequency of oscillations as also

seen in the experiment.

[1] T. Baumert, V. Engel, C. Röttgermann, W.T. Strunz, and G. Gerber, *Chem. Phys. Lett.* **191**, 639 (1992).

[2] P. Claas, G. Droppelmann, C. P. Schulz, M. Mudrich, and F. Stienkemeier, *J. Phys. B: At. Mol. Opt. Phys.* **39**, 1151 (2006).

[3] R. de Vivie-Riedle, B. Reischl, S. Rutz, and E. Schreiber, *J. Phys. Chem.* **99**, 16829 (1995).

MO 22.3 Do 16:30 Poster C1

Exact Wave-Packet Propagation for a Field Coupled Molecular System Employing a Perturbative Expansion — ●CIPRIAN PADURARIU¹, PHILIPP MARQUETAND², VOLKER ENGEL², and ULRICH KLEINEKATHÖFER¹ — ¹Jacobs University Bremen, Campus Ring 1, 28759 Bremen, Germany — ²Institut für Physikalische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

A method for solving the time-dependent Schrödinger equation numerically for a field coupled two electronic state system is presented. In each state, wave packets are propagated using the established split-operator technique. However, the transitions between the electronic surfaces are not treated within the standard generalization of this method to the two state problem which involves numerical evaluations of trigonometrical functions at each instant of time. In the proposed approach, the coupling is treated within time-dependent perturbation theory. The method relies on the observation that the perturbation wave function at time $t + dt$ can be obtained directly from the one at time t . A re-summation of the individual orders at each timestep dt is not necessary. Numerical results on a one-dimensional model system prove the robustness of the method, also exhibiting savings of approximately 35% in computation time compared to the standard split-operator technique for two surfaces. This is in particular important for higher dimensional systems where the computational effort is drastically reduced.

MO 22.4 Do 16:30 Poster C1

Circular Dichroism and absorption spectroscopy of merocyanine dimer aggregates: molecular properties and exci-

ton transfer dynamics from time-dependent*quantum calculations — ●JOACHIM SEIBT¹, ANDREAS LOHR², FRANK WÜRTHNER², and VOLKER ENGEL¹ — ¹Institut für Physikalische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg — ²Institut für Organische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

A wave packet approach to the calculation and interpretation of circular dichroism (CD) spectra is applied to the spectroscopy of aggregates of a merocyanine dye. A combined analysis of absorption and CD spectra allows for the extraction of geometric information and excited state electronic coupling. It is shown that in the case of dimer aggregates of a chiral merocyanine dye, it is possible to infer the dynamics of an exciton transfer directly from the CD spectrum. This relation is established via the Fourier relation to a time-dependent correlation function reflecting the quantum dynamics in the dye aggregate.

MO 22.5 Do 16:30 Poster C1

Absorption und Energietransfer von molekularen Aggregaten — ●JAN RODEN, GEORG SCHULZ, ALEXANDER EISFELD and JOHN BRIGGS — Theoretische Quantendynamik, Hermann-Herder-Str. 3, 79104 Freiburg

Unter Verwendung der CES-Näherung (Coherent Exciton Scattering) [1], bei der der exakte Greensoperator der Monomere durch ein Mittel über den Vibrationsgrundzustand ersetzt wird, können experimentelle Aggregat-Spektren mit sehr guter Übereinstimmung direkt aus dem gemessenen Monomer-Spektrum berechnet werden [2]. Es lassen sich die verschiedenen Linienformen des blauverschobenen H-Bandes und des extrem schmalen, rotverschobenen J-Bandes auf einfache Weise erklären. Insbesondere erhalten wir den exponentiellen Abfall der langwelligeren Flanke des J-Bandes (Urbach-Martienssen Regel) analytisch aus der Form des Monomer-Spektrums in diesem Energie-Bereich [3].

Desweiteren untersuchen wir den Einfluss von Vibrationen auf den Energietransfer in molekularen Aggregaten.

[1] J.S. Briggs, A. Herzenberg *J. Phys. B* **3**, 1663 (1970) [2] A. Eisfeld and J.S. Briggs, *Chem. Phys.* **324**, 376 (2006) [3] A. Eisfeld and J.S. Briggs, *Chem. Phys. Lett.* **446**, 354 (2007)

MO 23: Experimentelle Techniken

Zeit: Donnerstag 16:30–19:00

Raum: Poster C1

MO 23.1 Do 16:30 Poster C1

Experimenteller Aufbau zur Untersuchung des Dissoziationsprozesses von H₂⁺ — ●SOPHIE KIRSCHNER¹, MATTHIAS ODENWELLER¹, MUSTAFA YILDIRIM², KYRA COLE¹, LOTHAR SCHMIDT¹, MARKUS SCHÖFFLER¹, LUTZ FOUCHAR¹, JASMIN TITZE¹, ZENGHU CHANG^{1,3}, HORST SCHMIDT-BÖCKING¹ und REINHARD DÖRNER¹ — ¹Institut für Kernphysik, Johann Wolfgang Goethe-Universität, Frankfurt am Main, — ²Institute of Graduate School of Natural and Applied Sciences, Afyonkarahisar Kocatepe University, Afyonkarahisar, Turkey — ³Department of Physics, Kansas State University, Manhattan, KS, USA

Vorgestellt wird ein Versuchsaufbau, um das Verhalten von H₂⁺-Ionen unter Einwirkung starker Laserfelder zu untersuchen. Eine Adaption der renomierten COLTRIMS-Technik (COLd Target Recoil Ion Momentum Spectroscopy) erlaubt hierbei die Detektion aller beteiligten Teilchen über den vollen Raumwinkel. Mittels eines Pump-Probe-Experimentes bei verschiedenen Delays ist eine zeitaufgelöste Messung des Dissoziationsprozesses möglich.

Besondere Herausforderungen bei der technischen Umsetzung liegen in der Fokussierung des Lasers auf den Ionenstrahl.

MO 23.2 Do 16:30 Poster C1

Optimization of Nano-Structured Surfaces for Surface-Enhanced Raman Scattering (SERS) — ●MALTE SACKMANN, TORSTEN BALSTER, VEIT WAGNER, and ARNULF MATERNY — Jacobs University Bremen, Germany

Surface-enhanced Raman scattering (SERS) in the visible spectral region is typically observed for molecules in the vicinity of nano-structured metal surfaces. Here, rough metal surfaces, metal colloid solutions (Sol) as well as metal tips cause a strong enhancement of the Raman signal. In consequence SERS is a suitable spectroscopic technique for the measurement of very low analyte concentrations.

In order to perform experiments leading to a better understand-

ing of the enhancement effect, reproducible SERS-active substrates are required. For this purpose, we have prepared surfaces with two-dimensional gold-dot arrays on silicon by means of e-beam lithography. Different substrates were produced as grating-like arrangement of gold nano dots. In order to find the optimum enhancement, spacing, size and shape as well as the thickness of the gold layers (dot height) were varied. Raman spectra were recorded using the excitation wavelengths 514 and 671 nm resulting in a signal enhancement of up to three orders of magnitude. The SERS substrates were more efficient for the red excitation wavelength by a factor of approx. 10.

In our contribution, results of these experiments are shown and the relationship between the structure parameters and the enhancement factors are discussed. An outlook evaluating possible applications in industry and analytics is given.

MO 23.3 Do 16:30 Poster C1

Raman Spectroscopy for the Characterization of Coffee — ●RASHA HASSANEIN, PATRICE DONFACK, MALTE SACKMANN, and ARNULF MATERNY — Jacobs University Bremen, Germany

Coffee is one of the most popular beverages around the world. The varieties of coffee are directly influenced by environmental conditions and by the various methods of processing especially roasting, which consequently affect the quality of coffee. The discrimination between coffee species and blends for the purpose of monitoring quality and detecting fraud is difficult, since the chemical composition of coffee varieties is complex and many parameters are influencing the quality. Therefore, it is necessary to find parameters suitable for the differentiation of coffee. Recently, we have proposed Raman spectroscopy as a possible way to characterize coffee varieties of different geographical origins and roasting degrees. This is achieved by analyzing the volatile fraction and key components of coffee. The amounts and composition of flavor precursors in green coffee have a dramatic effect on the quality of the final roasted coffee. For example, trigonelline - which is common in raw coffee beans - plays a significant role not only in forming the aroma

and flavor but also since antioxidant chemicals are formed during the roasting process. We have taken Raman spectra and analyzed them in order to identify trigonelline in green coffee from different geographical regions. Additionally, we have taken spectra of vapor extractions from coffees based on freshly grounded beans as well as from instant coffee. Clear differences could be detected, which are discussed with respect to their importance in assessing the quality of coffee.

MO 23.4 Do 16:30 Poster C1

Erzeugung und Formung von ultrabreitbandigen fs-Laserpulsen im sichtbaren Spektralbereich — •TATJANA LÖHRIG^{1,2}, FLORIAN LANGHOJER^{1,2}, FRANK DIMLER^{1,2} und TOBIAS BRIXNER^{1,2} — ¹Institut für Physikalische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg — ²Physikalisches Institut, Universität Würzburg, Am Hubland, 97074 Würzburg

Die hier vorgestellten ultrabreitbandigen fs-Laserpulse werden mit Hilfe eines zweistufigen nichtkollinearen optisch-parametrischen Verstärkers (NOPA) erzeugt und decken den kompletten Spektralbereich von 500 nm bis 750 nm ab.

Zur Formung dieser Pulse dient ein zweischichtiges LCD mit jeweils 640 Pixeln, das sich in der Fourierebene eines Nulldispersionskompressors befindet. Die spektrale Aufspaltung der Pulse erfolgt durch holografisch geschriebene Volumenphasengitter (VPHG), die über den gesamten Spektralbereich eine hohe Effizienz aufweisen.

Zur Charakterisierung der Pulse wird ein transient grating FROG verwendet, bei dem die Phasen Anpassung für alle Frequenzanteile erfüllt ist. Gezeigt werden die gemessenen FROG traces sowohl für ungeformte als auch für geformte fs-Laserpulse. Als erstes Beispiel soll die Komprimierung eines Pulses mit Hilfe eines evolutionären Algorithmus gezeigt werden.

MO 24: Kalte Moleküle

Zeit: Donnerstag 16:30–19:00

Raum: Poster C1

MO 24.1 Do 16:30 Poster C1

Anion molecule reaction dynamics — •RICO OTTO, JOCHEN MIKOSCH, SEBASTIAN TRIPPEL, CHRISTOPH EICHHORN, PETR HLAVENKA, MATTHIAS WEIDEMÜLLER, and ROLAND WESTER — Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg

Anion-molecule reaction processes are known for their rich reaction dynamics, caused by a complex potential energy surface. We have carried out the first kinematically complete study of the S_N2 reaction of $Cl^- + CH_3I$ using crossed molecular beam imaging [1]. Different reaction mechanisms are observed as a function of collision energy. Currently, we study molecular dissociation dynamics in strong laser fields. In addition our experimental approach for the study of reactive scattering with laser aligned molecules will be discussed.

Slow collisions of anions at fixed temperature are also investigated in a 22pole radio frequency trap. We could identify evaporation of stored ions as the ultimate loss channel in this trapping device [2]. Proton transfer from H_2 to NH_2^- showed unexpected low temperature characteristics in the reaction rate coefficient. Ab initio calculations were carried out in order to explain this behaviour. The absolute cross section of OH^- photodetachment was measured using a tomography scan [3]. Two-dimensional tomography scans at different temperatures reveal further details of the ion density distribution.

[1] J. Mikosch *et al.*, Science (in press)

[2] J. Mikosch *et al.*, Phys. Rev. Lett. **98**, 223001 (2007)

[3] S. Trippel *et al.*, Phys. Rev. Lett. **97**, 193003 (2006)

MO 24.2 Do 16:30 Poster C1

A planar multipole ion trap for spectroscopy of water clusters — •CHRISTIAN GREVE¹, MICHAEL KRÖNER², MARKUS DEBATIN¹, JOCHEN MIKOSCH¹, SEBASTIAN TRIPPEL¹, MARKUS REETZ-LAMOUR¹, PETER WOIAS², ROLAND WESTER¹, and MATTHIAS WEIDEMÜLLER¹ — ¹Physikalisches Institut, Universität Freiburg — ²Institut für Mikrosystemtechnik, Universität Freiburg

Microhydrated ions provide the opportunity to study solvent effects such as reaction rates and ionisation potentials as a function of the solvation number and are subject to numerous theoretical and experimental investigations. We plan to perform spectroscopy in a planar chip trap providing an almost rectangular multipole trapping potential [1]. For good optical access the trap consists of two opposing glass chips each with an electrode structure which can be made transparent using indium tin oxide. For the creation of water cluster ions we have designed a source composed of an electron gun, a pulsed valve and an electrostatic lens in a small differentially pumped vacuum chamber. Detection after storage is accomplished by a Wiley-McLaren type spectrometer setup. For future experiments with water cluster ions we will implement a quadrupole filter for mass selective loading, which will eventually be integrated onto the same chip with the trap. In addition, we will combine the trap with a magneto optical trap for experiments on interactions of trapped ions with ultracold atoms.

[1] M. Debatin *et al.*, in prep.

[2] J. Mikosch *et al.*, Phys. Rev. Lett. **98**, 223001 (2007)

MO 24.3 Do 16:30 Poster C1

Stark deceleration of SO_2 — •OLEG BUCICOV¹, EBERHARD TIEMANN¹, and CHRISTIAN LISDAT² — ¹Institut für Quantenoptik, Leibniz Universität Hannover — ²Physikalisch-Technische Bundesanstalt, Braunschweig

We present a Stark decelerator for low-field-seeking states with 326 stages, with which we succeeded in decelerating SO_2 molecules to the velocity of about 50 m/s [1]. With this decelerator it should be possible to bring the relatively heavy SO_2 molecules to a standstill and to trap them electrostatically.

This offers the possibility of studying the predissociation of the trapped cold SO_2 at the threshold resulting in the production of cold SO molecules and O atoms. We will measure the velocity distribution of the photofragments. The previous research showed that the dissociation process can be manipulated by an external electric field that shifts the dissociation asymptotes relative to the predissociating levels [2]. In this way the reaction channels can be opened or closed at will or the tuning of the velocity of fragments can be attained, these opportunities being very attractive for the field of cold molecules and cold chemistry.

[1] O. Bucicov *et al.*, submitted to EPJD.

[2] S. Jung *et al.*, J. Phys. B **39**, S1085, 2006.

MO 24.4 Do 16:30 Poster C1

Production of a continuous guided beam of slow and internally cold molecules from a cryosource — •CHRISTIAN SOMMER, LAURENS VAN BUUREN, SEBASTIAN POHLE, MICHAEL MÖTSCH, JOSEPH BAYERL, PEPLIJN PINKSE, and GERHARD REMPE — Max-Planck-Institut für Quantenoptik, Hans-Kopfermann-Str. 1, 85748 Garching

Dense samples of cold polar molecules offer new perspectives in physics [1]. Studies of cold collisions and chemical reactions as well as high precision measurements will benefit from these samples. Further cooling to the ultracold regime will lead to conditions where the long range and anisotropic dipole-dipole interaction becomes dominant and new phenomena could be observed.

We have developed a new source delivering a continuous beam of slow and internally cold polar molecules. In the source room-temperature ND_3 molecules are injected into a cryogenic helium buffer gas where they are cooled in all degrees of freedom [2]. A fraction of the cold molecules is extracted by an electric quadrupole [3] and transported to a high-vacuum region outside the cryogenic source where it can, for example, be loaded into an electrostatic trap [4]. We will discuss the principle of operation, details of the set up, and present data of its performance.

[1] J. Doyle *et al.*, Eur. Phys. J. D **31**, 149 (2004)

[2] J.D. Weinstein *et al.*, Nature (London) **395**, 148 (1998)

[3] T. Junglen *et al.*, Eur. Phys. J. D **31**, 365 (2004)

[4] T. Rieger *et al.*, Phys. Rev. Lett. **95**, 173002 (2005)

MO 24.5 Do 16:30 Poster C1

Aufbau einer Stark-Effekt geführten Quelle für langsame Moleküle — •ADAM PIECHACZEK, MICHAEL STOLLE und HANS-PETER HELM — Molekül- und Optische Physik, Physikalisches Institut, Stefan-Meier-Str. 19, 79104 Freiburg

Mit dem Ziel langsame Moleküle in einer optischen Dipolfalle zu fangen

und dort sympathetisch mit kalten Alkali-Atomen zu kühlen, haben wir nach dem Vorbild [1] eine Apparatur zur Selektion und Führung langsamer Moleküle aufgebaut. Dabei werden mittels eines zweimal um 90 Grad gebogenen Vierpols in drei differentiellen Pumpstufen neutrale, polare Moleküle anhand des Stark-Effekts geführt, bzw. schnelle Moleküle ausgefiltert. Um zuletzt auch die innere Energie der Moleküle zu erniedrigen, wird dem langsamen Molekülstrahl am Ende des Vierpols räumlich eine Dipolfalle, gefüllt mit kalten Rb-Atomen, überlagert. Dort sollen sehr tiefe Temperaturen und damit hochauflösende Molekül-Spektroskopie sowie Untersuchung langsamer interner Prozesse gefangener Moleküle möglich werden. Momentan wird im ersten Schritt versucht, fluoreszierende Moleküle durch den Vierpol zu leiten, um über LIF zeitlich aufgelöst ihren inneren Zustand und ihre Bewegung zu verfolgen. In diesem Zusammenhang wollen wir auch koaxiale Laser-Spektroskopie am Stark-geführten Molekülstrahl durchführen um die Anfangsbedingungen der zur Kühlung vorliegenden Moleküle zu ermitteln.

[1] T. Rieger et al., Eur. Phys. J. D 31, 365 (2004), T. Junglen et al. PRL 92 223001, (2004)

MO 24.6 Do 16:30 Poster C1

Imino Tautomers of Gas Phase Guanine from Mid-Infrared Laser Spectroscopy — KAI SEEFELD, ROBERT BRAUSE, ●THOMAS HÄBER, and KARL KLEINERMANN — Institut für Physikalische Chemie, Heinrich-Heine Universität Düsseldorf, 40225 Düsseldorf, Germany

We reinvestigated the assignment of the three major guanine conformers detected via resonance enhanced two-photon ionization (R2PI) in supersonic expansions and present IR/UV double resonance spectra in the spectral region between 1500 and 1800 cm^{-1} . Comparison with B3LYP/TZVPP and RI-MP2/cc-pVQZ calculations shows that both conformers B and C are 7H-keto tautomers with an imine group in 2-position. They differ only in the local conformation of the imine group, but are otherwise identical. Conformer A is an amino-enol form with the OH group in trans position.

MO 24.7 Do 16:30 Poster C1

Conveyor belt for single molecular ions starts moving — ●STEFFEN KAHRA, GÜNTHER LESCHHORN, and TOBIAS SCHAETZ — Max-Planck-Institut für Quantenoptik, Garching

Recent and ongoing endeavours for growingly precise measurements of

time dependent structural properties of molecules have raised interest in better adapted target preparation methods. This can be understood as it might be crucial to extend existing methods to the few femtosecond or attosecond time scale. The experimental scheme we present aims for a fully controllable emitter of molecular ions. By exploiting the collected advantages of a linear Paul trap, sympathetic cooling schemes, light pressure separation of different ion species, field free alignment and a tunable reloading mechanism we might be able to position external cold and aligned molecular ions to a precision of about one micrometer at a repetition rate of up to 10 kHz inside a linear Paul trap. These targets seem to be suited for ultrafast electron diffraction and/or cold chemistry experiments. We will discuss the ability to incorporate those methods and can possibly comment on first results. The project is part of the excellence initiative MAP, financial support by MPG and IMPRS-APS is acknowledged.

MO 24.8 Do 16:30 Poster C1

Core hole localization von N_2 — ●MARKUS SCHÖFFLER¹, JASMIN TITZE¹, NIKOS PETRIDIS¹, TILL JAHNKE¹, KYRA COLE¹, LOTHAR SCHMIDT¹, ACHIM CZASCH¹, DOMINIQUE AKOURY¹, JOSHUA WILLIAMS⁵, NIKOLAI CHEREPKOV³, SERGEY SEMENOV³, BILL MCCURDY², TOM RESCIGNO², LEW COCKE⁴, TIMUR OSIPOV², SUN LEE², MIKE PRIOR², ALI BELKACEM², ALLEN LANDERS⁵, HORST SCHMIDT-BÖCKING¹, THORSTEN WEBER² und REINHARD DÖRNER¹ — ¹Institut für Kernphysik, Frankfurt, Deutschland — ²Lawrence Berkeley National Laboratory, Berkeley, USA — ³State University of Aerospace Instrumentation, St. Petersburg, Russland — ⁴Department of Physics, Kansas State University, USA — ⁵Department of Physics, Auburn University, USA

Seit Jahrzehnten diskutieren Physiker und Chemiker ob eine durch Photoabsorption erzeugte Innerschalenvakanz ein lokalisiertes Loch oder einen delokalisierten Quantenzustand hinterlässt. Wir haben dieses Problem anhand der Absorption von 419 eV zirkular polarisierten Photonen in N_2 -Moleküls untersucht. Mit einem speziell auf diese Frage abgestimmten Impulsspektrometer (COLTRIMS) konnten erstmals Photoelektron (10 eV), Augerelektron (400 eV) und die beiden Stickstoff-Rückstoßionen (5 eV) in Koinzidenz detektiert werden. Zusammen mit theoretischen Rechnungen kann zum ersten Mal überhaupt gezeigt werden, dass wie Symmetriebrechung bzw. deren -erhaltung zusammenhängen; letztendlich ist dies eine Ergebnis aus dem Zerfall eines verschränkten Bell-Zustandes.

MO 25: Cluster

Zeit: Donnerstag 16:30–19:00

Raum: Poster C1

MO 25.1 Do 16:30 Poster C1

Photoionization of He Dimers — ●TILO HAVERMEIER, TILL JAHNKE, ROBERT GRISENTI, KATHRINA KREIDI, MARKUS SCHÖFFLER, SVEN SCHÖSSLER, NADINE NEUMANN, JASMIN TITZE, MATHIAS KÜHNEL, JÖRG VOIGTSBERGER, HENDRIK SANN, ROBERT WALLAUER, STEFAN VOSS, FELIX STURM, LUTZ FOUCHAR, JUAN MORILLAS, HORST SCHMIDT-BÖCKING, and REINHARD DÖRNER — Institut für Kernphysik, University Frankfurt, Max von Laue Str. 1, 60438 Frankfurt, Germany.

The helium dimer is one of the most weakly bound systems in the universe. This makes it an interesting quantum mechanical object for investigation. These Van der Waals Clusters can be produced in an expansion of a cryogenic gas jet through a small nozzle into vacuum. In the present experiment we examine the interaction of He dimers with synchrotron radiation at an energy range from 64 to 78 eV. We observed different pathways leading to single ionization of both He atoms of the dimer compound. This two close standing ions begin now to dissociate in cause of their coulomb potential. All charged fragments were detected in coincidence with a COLTRIMS system. Especially Interatomic Coulombic Decay (ICD) and the two step process (TS1) were clearly identified. Furthermore a distribution of the internuclear distance was obtained from the measured Kinetic Energy Release (KER).

MO 25.2 Do 16:30 Poster C1

Elektronenspektroskopie an Wasserclustern — ●MARKO FÖRSTEL, SILKO BARTH, VOLKER ULRICH, TORALF LISCHKE, MELANIE MUCKE und UWE HERGENHAHN — Max-Planck-Institut für Plasma-physik, EURATOM association, Boltzmannstr. 2, 85748 Garching

In schwach gebundenen (van der Waals oder H-Brücken) Clustern sind Autoionisationsprozesse möglich, die direkt in einen Zustand mit zwei positiven Ladungen an zwei verschiedenen Konstituenten führen. Dieser Mechanismus ist als Interatomarer oder Intermolekularer Coulomb Zerfall (ICD) bekannt geworden. Der Vorhersage nach läuft er in sehr vielen Arten von Clustern ab, gut erforscht ist er aber bis jetzt nur für die van der Waals Cluster aus Edelgasen. Im Poster werden erste Hinweise auf ICD in Wasser gezeigt.

Dotierte Wasser-Cluster sind ebenfalls von großem Interesse, da sie als Modell für die Solvatation von Substanzen in flüssigem Wasser dienen können. In dem Beitrag wird ein neuer Aufbau zur Herstellung alkali-dotierter, positiv geladener Wasser-Cluster vorgestellt und erste experimentelle Ergebnisse diskutiert.

MO 25.3 Do 16:30 Poster C1

Untersuchung der Lokalisation von K-Schalen Photoelektronen in Neon-Dimeren — ●K. KREIDI^{1,2}, T. JAHNKE¹, T. WEBER³, T. HAVERMEIER¹, R. GRISENTI¹, X.-J. LIU⁴, Y. MORISITA⁵, S. SCHÖSSLER¹, L. SCHMIDT¹, M. SCHÖFFLER¹, M. ODENWELLER¹, N. NEUMANN¹, L. FOUCHAR¹, J. TITZE¹, B. ULRICH¹, F. STURM¹, C. STUCK¹, R. WALLAUER¹, S. VOSS¹, I. LAUTER¹, H.-K. KIM¹, M. RUDLOFF¹, H. FUKUZAWA⁴, G. PRÜMPER⁴, N. SAITO⁵, K. UEDA⁴, A. CZASCH¹, O. JAGUTZKI¹, H. SCHMIDT-BÖCKING¹, S. K. SEMENOV⁶, N.A. CHEREPKOV⁶ und R. DÖRNER¹ — ¹Institut für Kernphysik, J. W. Goethe Universität, Max-von-Laue-Str. 1, 60438 Frankfurt, Germany — ²DESY, Notkestrasse 85, 22607 Hamburg, Germany — ³Lawrence Berkeley National Laboratory, Berkeley CA 94720, USA — ⁴Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan — ⁵National Metrology Institute of

Japan, AIST, Tsukuba 305-8568, Japan — ⁶State University of Aerospace Instrumentation, 190000 St. Petersburg, Russia

Mit der COLTRIMS-Technik wurde der Zerfall von Neondimeren nach der K-Schalen-Ionisation mit einer Photonenenergie von 881.2 eV untersucht. Die Zerfallsmechanismen, die zu den Aufbrüchen des Dimers (Ne^+/Ne^+ und $\text{Ne}^+/\text{Ne}^{2+}$) führen, wurden identifiziert. Die Lokalisation des K-Schalen Photoelektrons wurde anhand der Symmetrie der Winkelverteilung um die Molekülachse untersucht. Die Winkelverteilung der ICD-Elektronen liefert durch ihre asymmetrische Struktur Aufschluss über die Art des ICD-Zerfalls.

MO 25.4 Do 16:30 Poster C1

Ligand-binding motifs in hydroxybenzene-ligand cation complexes — ALEXANDER PATZER, HARALD KNORKE, JUDITH LANGER, and •OTTO DOPFER — Institut für Optik und Atomare Physik, TU Berlin, Hardenbergstrasse 36, 10623 Berlin

The competition between hydrogen-bonding and π -stacking is of fundamental importance for molecular recognition. In this contribution, we present IR spectroscopic and quantum chemical results for resorcinol cation complexes with inert ligands (e.g., Ar, N₂). IR spectra of mass-selected complexes are obtained via photodissociation in a tandem mass spectrometer [1]. The combined spectroscopic and quantum chemical approach provides detailed insight into the preferred ion-ligand binding motif, the actual binding site (isomer), and the strength of the intermolecular bond as a function of the ligand type, the number of ligands, and the resorcinol isomer. Comparison with the corresponding phenol complexes [2] reveals the effects of the second hydroxy group on the intermolecular interaction potential.

[1] O. Dopfer, *Int. Rev. Phys. Chem.* **22**, 437 (2003).

[2] O. Dopfer, *Z. Phys. Chem.* **219**, 125 (2005).

MO 25.5 Do 16:30 Poster C1

Nonclassical versus classical structures of the ethyl cation probed by IR spectroscopy — HORIA-SORIN ANDREI, NICOLA SOLCA, and •OTTO DOPFER — Institut für Optik und Atomare Physik, TU Berlin, Hardenbergstrasse 36, 10623 Berlin

The competition between classical and nonclassical geometries is a fundamental issue for hydrocarbon molecules. The ethyl cation (C₂H₅⁺, protonated ethene) represents the most simple example for protonation of a C=C double bond. Calculations predict the nonclassical structure to be slightly more stable than the classical structure. However, spectroscopic evidence for this conclusion is still lacking. The present work

reports IR photodissociation spectra [1] of size selected clusters of the ethyl cation with Ar, N₂, CO₂, and CH₄. The IR spectra recorded in the CH stretching range provide detailed information on the degree of delocalization of the excess proton between the two C atoms. Significantly, the structure of the additional proton depends sensitively on the microsolvation environment. Whereas Ar is a negligible perturber [2], leaving C₂H₅⁺ in the most stable nonclassical geometry, the stronger interaction with N₂ induces a switch from a nonclassical to a classical C₂H₅⁺ ion core. The latter ligand appears to form a weak covalent bond to one C atom of the ethyl cation. The interpretation of the IR spectra is supported by rotational line profile simulations and ab initio calculations.

[1] O. Dopfer, *Int. Rev. Phys. Chem.* **22**, 437 (2003). [2] H.S. Andrei, N. Solca, O. Dopfer, *Angew. Chem.*, in press, DOI: 10.1002/anie.200704163 (2007)

MO 25.6 Do 16:30 Poster C1

Electronic structure and optical properties of ideal diamond clusters - diamondoids — LASSE LANDT¹, KATHRIN KLÜNDER¹, •MATTHIAS STAIGER¹, JEREMY DAHL², ROBERT CARLSON², THOMAS MÖLLER¹, and CHRISTOPH BOSTEDT¹ — ¹Technische Universität Berlin, Germany — ²MolecularDiamond Technologies, Richmond (CA), USA

Diamondoids can be considered a new form of ideal diamond clusters in the (sub-)nanometer size regime. Because they can be perfectly size and isomer selected fundamental investigations about size and shape effects in neutral clusters known with atomic precision are now becoming possible.

We have investigated highest occupied and lowest unoccupied states as well as optical absorption across the gap for a series of diamondoids from adamantane up to hexamantane. The combination of these three investigations paints a comprehensive picture of their electronic structure. All experiments have been performed in the gas phase reproducing the same idealized boundary conditions of interaction-free and neutral clusters typically assumed in theoretical investigations.

We find that the lowest unoccupied states do not show any particle size. The highest occupied states, however, show strong size but only minor isomeric dependencies. These findings are explained with the localization of the lowest unoccupied states on the surface and the highest occupied states in the core of the cluster. The absorption measurements across the gap in the VUV energy regime reveal strong changes of the spectra with the particle shape and symmetry.

MO 26: Spektroskopie in He-Tröpfchen

Zeit: Donnerstag 16:30–19:00

Raum: Poster C1

MO 26.1 Do 16:30 Poster C1

Microsolvation of alkali metals in H₂O, NH₃ studied by photoionisation in helium nanodroplets — •SEVERIN MÜLLER¹, MARCEL MUDRICH¹, FRANK STIENKEMEIER¹, and UDO BUCK² — ¹Universität Freiburg, Physikalisches Institut, D-79104 Freiburg, Germany — ²Max-Planck-Institut für Dynamik und Selbstorganisation, D-37073 Göttingen, Germany

Helium nanodroplets have proven to be a valuable tool for the study of tailor-made species assembled within the droplets. We apply helium nanodroplet isolation spectroscopy to study the microsolvation of alkali metal clusters in the polar solvents water and ammonia. The droplets are doped consecutively with solvent molecules and alkali atoms. Further downstream they are nonresonantly ionized by a Ti:Sa femtosecond oscillator or electron bombardment. The mass distribution of products is analyzed using a high-resolution quadrupole mass spectrometer. From the mass spectra numerous compounds of the alkali atom and different water-related particles like O, OH, H₂O are identified and their relative intensities discussed. By comparing PI spectra of different products ion chemical reactions induced by the ionization can be separated from reactions occurring already in the cold (0.4K) superfluid helium matrix. Comparison with similar studies carried out in molecular beams [1] allows us to characterize the influence of the matrix on the solvation and ionization process.

[1] C. Steinbach, U. Buck: Reaction and solvation of sodium in hydrogen bonded solvent clusters. *Phys. Chem. Chem. Phys.* **2005**, *7*, 986

MO 26.2 Do 16:30 Poster C1

Localisation of Calcium in ³He, ⁴He and mixed ³He/ ⁴He Nanodroplets — •MATTHIEU DVORAK, OLIVER BÜNERMANN, and FRANK STIENKEMEIER — Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg-im-Breisgau

Electronic spectroscopy of atomic impurities in helium nanodroplets is a sensitive method for determining the localisation of the impurity in the droplet. The important observables are the shift as well as the width of electronic transitions. Atomic impurities located inside the droplet show large blue shifts identical to measurements made in bulk helium. Atomic impurities located on the surface, for example alkali metal atoms, only show small blue shifts.

We present new results of the $4s^2\ ^1S_0 \leftarrow 4s4p\ ^1P_0$ transition of calcium atoms bound to droplets formed of both helium isotopes. The results are directly compared to those obtained in bulk helium. For ⁴He the shift is much smaller in the droplet than in bulk but for helium ³He shifts are the same in both cases. The interpretation that calcium is located in the centre of the ³He droplet and on the surface of ⁴He droplets agrees with the prediction of theoretical calculations and is consistent with results obtained for strontium[1].

Calcium in ³He-⁴He mixed droplets have also been studied. The aim of this experiment is to map out a situation where calcium is located at the interface of ⁴He and ³He.

[1] A. Hernando, R. Mayol, M. Pi, M. Barranco, F. Ancilotto, O. Bünermann and F. Stienkemeier, *J. Phys. Chem. A*, **2007**, *111*, 7303-7308

MO 26.3 Do 16:30 Poster C1

Solvation of HCl - aggregation of H₂O, HCl and their deuterated isotopes in superfluid He droplets — MARKUS ORTLIEB, ÖZGÜR BIRER, GERHARD SCHWAAB, ANNA GUTBERLET, and MARTINA HAVENITH — Department of Physical Chemistry II, Ruhr-University Bochum, Universitätsstr. 150, D-44780

We investigate aggregates of HCl, H₂O and their deuterated isotopes embedded in superfluid helium using a helium nanodroplet spectrometer combined with an infrared OPO set up with an output power of up to 2.7 W and a resolution of better than 0.001 cm⁻¹. Depletion spectra of the super cooled aggregates (0.37 K) were recorded between 2650 cm⁻¹ and 2720 cm⁻¹. We were able to assign the HCl stretch vibration of the HCl-H₂O complex. We also observed spectral features of (HCl)_m(H₂O)_n aggregates and isotopes in the region of the H₃O⁺ stretch vibration. We have investigated the question of how many H₂O molecules are needed to solvate HCl. Therefore we detected the pressure dependent intensity of the signal and did mass selective spectroscopy.

MO 26.4 Do 16:30 Poster C1

IR-spectroscopy of sulfuric acid in liquid He nanodroplets — MELANIE LETZNER, ÖZGÜR BIRER, and MARTINA HAVENITH — Department of Physical Chemistry II, Ruhr-Universität Bochum, Universitätsstraße 150, D-44780 Bochum, Germany

We investigate deuterated sulfuric acid and aggregates with water at ultracold temperatures in helium-nanodroplets in the range from 2650-2680 cm⁻¹. Helium nanodroplets are formed by expansion of helium at 40 bar through a 5 μm nozzle which is kept at a temperature of 16 K.

Under these conditions clusters with an average size of 5400 atoms are formed. Measurements were carried out using a high power IR-OPO (cw: 2.7 W) as radiation source. We were able to record rotationally resolved spectra which yield important information on the inherent structure.

MO 26.5 Do 16:30 Poster C1

Löslichkeit von Magnesium in Heliumtropfen — SEBASTIAN GÖDE, ANDREAS PRZYSTAWIK, JOSEF TIGGESBÄUMKER und KARL HEINZ MEIWES-BROER — Universität Rostock, Institut für Physik, Universitätsplatz 3, 18051 Rostock

Bei einer Düsenstrahlexpansion von Helium ins Vakuum entstehen ultrakalte Heliumtröpfchen, die beim Passieren einer Pickup-Zelle Atome aus einem Dampf niedriger Dichte aufnehmen können. Ob sich die Atome nach dem Pickup auf der Tropfenoberfläche oder im Tropfen befinden, hängt von Ihrer Wechselwirkung mit dem Helium ab.

Für das Verhalten der Elemente der Erdalkalimetalle ist eine genaue Vorhersage im Rahmen des Modells von Ancilotto [1] nicht möglich. Experimente haben gezeigt, dass Ca, Sr und Ba einen stabilen Zustand an der Oberfläche der Heliumtropfen haben. Für Magnesium hingegen gibt es kontroverse experimentelle Ergebnisse [2,3]. In diesem Beitrag werden Resultate zwei unterschiedlicher experimenteller Zugänge vorgestellt. Optische Anregungsspektren von Mg-Atomen werden der energieabhängigen Ionenausbeute der Elektronenstoßionisation gegenübergestellt und die unterschiedlichen Ionisationsmechanismen diskutiert.

[1] F. Ancilotto *et al.*, J. Low Temp. Phys. **101**, 1123 (1995)

[2] J. Reho *et al.*, J. Chem. Phys. **112**, 8409 (2000)

[3] Y. Ren and V.V. Kresin, Phys. Rev. A **76**, 043204 (2007)