

## MOLEKÜLPHYSIK (MO)

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 ÜBERSICHT DER HAUPTVORTRÄGE UND FACHSITZUNGEN  
 (Hörsäle H10 und H12)

## Hauptvorträge

MO 21.1	Di	10:40	(H12)	Molecules in Electronic Circuits: from integrated single molecules to SAMs in CMOS technology, <u>Marcel Mayor</u>
MO 21.2	Di	11:10	(H12)	Single-molecule electronics: Conductance mechanisms, <u>Gianaurelio Cuniberti</u>
MO 41.1	Mi	10:40	(H12)	Light and molecules: from structure to function using laser pulses, <u>Leticia González</u>
MO 41.2	Mi	11:10	(H12)	Ultrafast bimolecular proton transfer in water: from direct exchange to sequential hopping, <u>Erik T. J. Nibbering</u> , Omar F. Mohammed, Jens Dreyer, Diana Pines, Ehud Pines
MO 41.3	Mi	11:40	(H12)	<i>o</i> -Nitrobenzaldehyde: A "Tool" to study Hydrogen Transfer Reactions, Nucleophilic Additions, and Eliminations, <u>Peter Gilch</u> , Hilmar Schachenmayr, Wolfgang Schreier, Stefan Laimgruber
MO 41.4	Mi	12:10	(H12)	Peptides and peptide aggregates in the gas phase: what do we learn from isomer selective IR/UV spectroscopy, <u>Markus Gerhards</u>

## Fachsitzungen

MO 11	VUV Spectroscopy	Mo	11:00–12:00	H10	MO 11.1–11.4
MO 12	Ultrafast Structural Changes	Mo	14:00–16:00	H12	MO 12.1–12.7
MO 13	Molecular Clusters I	Mo	14:00–16:00	H10	MO 13.1–13.8
MO 14	Ultrafast IR and Raman Probe and Control	Mo	16:30–18:30	H12	MO 14.1–14.8
MO 15	Molecular Clusters II	Mo	16:30–18:45	H10	MO 15.1–15.9
MO 21	Molecular Electronics and Energy Transfer	Di	10:40–12:40	H12	MO 21.1–21.6
MO 22	Spectroscopy in He-Droplets	Di	11:40–12:40	H10	MO 22.1–22.4
MO 23	Photochemistry	Di	14:00–16:00	H12	MO 23.1–23.8
MO 24	High Resolution Spectroscopy	Di	14:00–16:00	H10	MO 24.1–24.8
MO 25	Poster: Electronic Spectroscopy	Di	16:30–18:30	Labsaal	MO 25.1–25.5
MO 26	Poster: Photochemistry	Di	16:30–18:30	Labsaal	MO 26.1–26.2
MO 27	Poster: Femtosecond Spectroscopy	Di	16:30–18:30	Labsaal	MO 27.1–27.12
MO 28	Poster: Quantum Control	Di	16:30–18:30	Labsaal	MO 28.1–28.7
MO 29	Poster: Biomolecules	Di	16:30–18:30	Labsaal	MO 29.1–29.2
MO 30	Poster: Quantum Chemistry	Di	16:30–18:30	Labsaal	MO 30.1–30.4
MO 31	Poster: Molecular Dynamics	Di	16:30–18:30	Labsaal	MO 31.1–31.2
MO 41	Hauptvorträge	Mi	10:40–12:40	H12	MO 41.1–41.4
MO 42	Excitation and Coherence Decay	Mi	14:00–16:00	H12	MO 42.1–42.8

MO 43	<b>Biomolecules I</b>	Mi 14:00–16:00	H10	MO 43.1–43.8
MO 44	<b>Quantum Chemistry and Molecular Dynamics</b>	Mi 16:30–18:15	H12	MO 44.1–44.7
MO 45	<b>Biomolecules II</b>	Mi 16:30–18:30	H10	MO 45.1–45.8
MO 51	<b>Molecular Quantum Control</b>	Do 10:40–12:40	H12	MO 51.1–51.8
MO 52	<b>Cold molecules I</b>	Do 10:40–12:40	H10	MO 52.1–52.7
MO 53	<b>Molecular Quantum Computing</b>	Do 14:00–16:00	H12	MO 53.1–53.6
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MO 55	<b>Poster: Collisions and Energy Transfer</b>	Do 16:30–18:30	Labsaal	MO 55.1–55.8
MO 56	<b>Poster: Molecular Clusters</b>	Do 16:30–18:30	Labsaal	MO 56.1–56.5
MO 57	<b>Poster: Cold Molecules</b>	Do 16:30–18:30	Labsaal	MO 57.1–57.11
MO 58	<b>Poster: Spectroscopy in He-Droplets</b>	Do 16:30–18:30	Labsaal	MO 58.1–58.3
MO 59	<b>Poster: Experimental Techniques</b>	Do 16:30–18:30	Labsaal	MO 59.1–59.3
MO 60	<b>Poster: Various Topics</b>	Do 16:30–18:30	Labsaal	MO 60.1–60.2
MO 71	<b>Dynamics and Spectroscopy at Interfaces</b>	Fr 10:40–12:25	H12	MO 71.1–71.7
MO 72	<b>Collisions and Energy Transfer</b>	Fr 10:40–12:40	H10	MO 72.1–72.8

### Mitgliederversammlung des Fachverbands Molekülphysik

Di 16:00–16:30 H10

1. Bericht des Vorsitzenden
2. Frühjahrstagung 2007 in Düsseldorf
3. Bericht vom Vorstandsrat und den Veränderungen in der DPG
4. Verschiedenes

## Fachsitzungen

– Haupt-, Fach-, Kurzvorträge und Posterbeiträge –

### MO 11 VUV Spectroscopy

Zeit: Montag 11:00–12:00

Raum: H10

MO 11.1 Mo 11:00 H10

**Two-Color Photoionization of Bromine** — ●JÜRGEN PLENGE<sup>1,2</sup>, CHRISTOPHE NICOLAS<sup>3</sup>, ALISON CASTER<sup>2</sup>, MUSA AHMED<sup>3</sup> und STEPHEN R. LEONE<sup>2,3</sup> — <sup>1</sup>Institut für Physikalische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg — <sup>2</sup>Departments of Chemistry and Physics, University of California, Berkeley, California 94720 — <sup>3</sup>Lawrence Berkeley National Laboratory, Berkeley, California 94720

Two-color photoionization of molecular bromine (Br<sub>2</sub>) has been studied by photoelectron spectroscopy using vacuum ultraviolet (VUV) synchrotron radiation and visible Nd:YLF laser light. The experiments were carried out on the Chemical Dynamics Beamline at the Advanced Light Source (Berkeley, USA). The second harmonic of the 1 kHz pulsed Nd:YLF laser was used to excite the  $X(^1\Sigma_g, v'' = 0) \rightarrow B(^3\Pi, v' = 28, 29)$  transitions of Br<sub>2</sub> near 527 nm. The long-lived B(<sup>3</sup>Π) state of Br<sub>2</sub> was ionized using VUV radiation in the photon energy range 8.5–10 eV. The ejected photoelectrons were detected utilizing a velocity map imaging detector and photoelectron energy distributions were measured. The obtained two-color photoionization spectra are compared with VUV one-color photoionization spectra. Distinct differences in the photoelectron kinetic energy distributions of both photoionization schemes are observed and discussed with the aid of Franck-Condon calculations.

MO 11.2 Mo 11:15 H10

**UV/VIS-Fluoreszenzspektroskopie von 2p-angeregtem Schwefelwasserstoff** — ●ROMAN FLESCHE<sup>1</sup>, JÜRGEN PLENGE<sup>1</sup>, MICHAEL MEYER<sup>2</sup> und ECKART RÜHL<sup>1</sup> — <sup>1</sup>Institut f. Physikalische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg — <sup>2</sup>LIXAM, Centre Universitaire Paris-Sud, Bat. 350, F-91898 Orsay Cedex, Frankreich

Die radiative Relaxation von Schwefelwasserstoff (H<sub>2</sub>S) nach Anregung im 2p-Nahkantenbereich wird mit Hilfe der UV/VIS - Spektroskopie untersucht. Dispergierte Undulatorstrahlung wird zur selektiven Erzeugung von 2p-angeregten Rydberg- und Valenzzuständen genutzt. Es werden ausgeprägte Unterschiede in den Fluoreszenzspektren in Abhängigkeit vom primären Anregungszustand beobachtet. Die Anregung von Rydbergzuständen führt nahezu ausschließlich zur Bildung leuchtender atomarer Fragmente (H, S<sup>+</sup>, S<sup>++</sup>). Die Anregung von Valenzzuständen liefert zusätzlich *molekulare* Banden, die dem Übergang A<sup>3</sup>Π → X<sup>3</sup>Σ<sup>-</sup> des einfach geladenen Photofragments HS<sup>+</sup> zugeordnet werden. Die beobachteten Banden werden im Hinblick auf die Fragmentationsdynamik der 2p-angeregten Valenzzustände diskutiert.

MO 11.3 Mo 11:30 H10

**Probing the dicationic final states in CO using KVV normal Auger transitions** — ●RALPH PÜTTNER<sup>1</sup>, XIA-JING LIU<sup>2</sup>, GEORG PRÜMPER<sup>2</sup>, TORALF LISCHKE<sup>2</sup>, VINCENZO CARRAVETTA<sup>2,3</sup> und KIYOSHI UEDA<sup>2</sup> — <sup>1</sup>Freie Universität Berlin, Institut für Experimentalphysik, Arnimallee 14, 14195 Berlin, Germany — <sup>2</sup>Inst. Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan — <sup>3</sup>IPCF- CNR, 56124 Pisa, Italy

It is well known that the KVV normal Auger spectra of CO subsequent to the C 1s and O 1s photoionization exhibit a rich vibrational fine structure, which is due to the fact that the resulting dications are stable with respect to dissociation. We present high-resolution normal Auger spectra together with the corresponding photoelectron spectra. All four spectra are fitted parallel using a Franck-Condon fit procedure which allows to take vibrational lifetime interference contributions into account. With this analysis we were able to identify for the first time contributions of the O 1s<sup>-1</sup> → X<sup>3</sup>Π Auger transition in the spectrum. In addition, the equilibrium distances, vibrational energies, and anharmonicities for the dicationic final states X<sup>3</sup>Π, a<sup>1</sup>Σ<sup>+</sup>, b<sup>1</sup>Π, A<sup>3</sup>Σ<sup>+</sup>, and d<sup>1</sup>Σ<sup>+</sup> were derived and compared with theoretical results [1]. While for the final states a<sup>1</sup>Σ<sup>+</sup>, b<sup>1</sup>Π, A<sup>3</sup>Σ<sup>+</sup>, and d<sup>1</sup>Σ<sup>+</sup> an excellent agreement between experiment and theory is found, we observe significant differences for the state X<sup>3</sup>Π. We assume that these differences are due to an avoided level crossing which is not taken into account in the calculations.

[1] J. H. D. Eland *et al.*, J. Phys. B **37**, 3197 (2004).

MO 11.4 Mo 11:45 H10

**Accidental predissociation of the N<sub>2</sub><sup>+</sup>(C<sup>2</sup>Σ<sub>u</sub><sup>+</sup>) state observed in the C<sup>2</sup>Σ<sub>u</sub><sup>+</sup> + X<sup>2</sup>Σ<sub>g</sub><sup>+</sup> fluorescence after vibrational selective excitation of the 1s<sup>-1</sup>π\* resonance** — ●L WERNER<sup>1</sup>, S KLUMPP<sup>1</sup>, A EHRESMANN<sup>1</sup>, PH DEMEKHIN<sup>2,3</sup>, M LEMESHKO<sup>2</sup>, V SUKHORUKOV<sup>2,3</sup>, K-H SCHARTNER<sup>4</sup>, and H SCHMORANZER<sup>3</sup> — <sup>1</sup>Institute of Physics, University of Kassel, D-34132 Kassel — <sup>2</sup>Rostov State University, 344038 Rostov-on-Don — <sup>3</sup>TU Kaiserslautern, D-67653 Kaiserslautern — <sup>4</sup>Justus-Liebig-University, D-35392 Giessen

N<sub>2</sub><sup>+</sup>(C - X) fluorescence was investigated by photon-induced fluorescence spectroscopy after vibrational selective excitation of the 1s<sup>-1</sup>π\* resonance in the fluorescence wavelength range between 135nm - 205nm. One peculiarity of the N<sub>2</sub><sup>+</sup>(C - X) fluorescence after direct excitation of the N<sub>2</sub><sup>+</sup>(C) state is the strong intensity decrease for bands with v' ≥ 3. In a first experiment only band sequences with Δv=const. could be observed but with an improved fluorescence resolution of 0.1nm it was possible to observe single fluorescence bands with Δv=-6/-7. Calculations predict a maximum of the fluorescence intensity at Δv = -5 if accidental predissociation is taken into account. With a very narrow fluorescence resolution of about 0.1nm it was even possible to resolve individual vibrational bands. Observed fluorescence intensities for the individual vibrational sequences of the C-X transition and measured cross sections of the C-X fluorescence for vibrational sequences were compared to calculations with taking into account accidental predissociation and molecular rotation. The calculated intensities and describe well the shape of both individual vibrational bands and the whole band system.

### MO 12 Ultrafast Structural Changes

Zeit: Montag 14:00–16:00

Raum: H12

#### Fachvortrag

MO 12.1 Mo 14:00 H12

**Bewegte Bilder auf atomarer Längen- und Zeitskala: Femtosekunden Röntgenbeugung** — ●MATIAS BARGHEER — Max-Born-Institut, Max-Born-Str. 2a, 12489 Berlin

Die Funktion vieler physikalischer Systeme von Molekülen über weiche Materie bis hin zu Festkörpern beinhaltet Veränderungen der Gleichgewichtsstruktur. Durch Röntgenbeugung lassen sich Strukturen auf atomarer Längenskala exakt vermessen. Die Zeitskala der mikroskopischen Veränderungen wird durch die relevanten Schwingungsmoden bestimmt

und liegt im Bereich von Femtosekunden bis Pikosekunden. Neuartige Quellen ultrakurzer Röntgenpulse - laserbasiert oder an Elektronenbeschleunigern - erreichen Pulsdauern von ca. 100 fs. Diese ultrakurze Belichtungszeit erlaubt es, den Ablauf einer strukturellen Veränderung durch Schnappschüsse zu verschiedenen Zeiten nach einer ultrakurzen Anregung des Systems zu filmen. Man kann somit einen selektiv angeregten, kohärenten Teil der Gitterdynamik beobachten, selbst wenn diese kollektive Bewegung eine kleinere Amplitude als die thermischen Fluktuationen hat. Anhand von drei Beispielen (Halbleiter-Nanostrukturen,

Ferroelektrika und Molekülkristalle) wird in diesem Vortrag gezeigt, welche Informationen man aus der Beobachtung der Dynamik in Echtzeit ziehen kann, und welche Perspektiven sich daraus für die Ultrakurzzeit-Molekülphysik ergeben.[1,2]

[1] M. Bargheer, N. Zhavoronkov, Y. Gritsai, J. C. Woo, D. S. Kim, M. Woerner, and T. Elsaesser, *Science* 306, 1771 (2004)

[2] M. Bargheer, N. Zhavoronkov, M. Woerner, T. Elsaesser, *Minireview in PhysChemPhys*, accepted (2006)

MO 12.2 Mo 14:30 H12

**Transiente Absorptionsspektroskopie an organischen Molekülkristallen aus DIABN** — ●CHRISTOPHER ROOT, PETER GILCH, MARKUS BRAUN und WOLFGANG ZINTH — Lehrstuhl für Biomolekulare Optik, Oettingenstrasse 67, Ludwig-Maximilians-Universität München, 80538 München

Die Molekülgruppe der Aminobenzonitrile kann nach Photoanregung einen intramolekularen Ladungstransfer durchführen. Diese Vorgänge können in den beiden Vertretern Dimethylaminobenzonitril (DMABN) und Diisopropylaminobenzonitril (DIABN) in Lösung mittels transienter Absorptionsspektroskopie sichtbar gemacht werden.

Im kristallinen Festkörper kommen zusätzlich beobachtbare Effekte hinzu. Diese führen zu Absorptionsänderungen, die über mehrere hundert Pikosekunden hinweg zerfallen. Durch geeignete Wahl der Anregungsbedingungen kann man deren Einfluss auf die messbaren Signale gezielt beeinflussen. Die gezeigten Ergebnisse dienen als Grundlage für zeitaufgelöste Röntgenbeugungsexperimente, bei denen unter gleichen experimentellen Voraussetzungen die Auswirkung des Ladungstransfers beobachtet werden kann.

MO 12.3 Mo 14:45 H12

**Ultrafast X-ray diffraction study of the molecular crystal DIABN** — ●CLEMENS VON KORFF SCHMISING<sup>1</sup>, MAREIKE KIEL<sup>1</sup>, MATIAS BARGHEER<sup>1</sup>, MICHAEL WOERNER<sup>1</sup>, THOMAS ELSAESSER<sup>1</sup>, CHRISTOPHER ROOT<sup>2</sup>, MARKUS BRAUN<sup>2</sup>, and WOLFGANG ZINTH<sup>2</sup> — <sup>1</sup>Max-Born-Institut, Max-Born-Str. 2a, 12047 Berlin — <sup>2</sup>Lehrstuhl für Biomolekulare Optik, Oettingenstrasse 67, Ludwig-Maximilians-Universität München, 80538 München

We present x-ray diffraction data taken on single crystals and powder samples of the molecular crystal diisopropylaminobenzonitrile (DIABN), recorded with a femtosecond x-ray plasma source providing a time-resolution of few 100 fs. DIABN represents a model system for photoinduced charge transfer, and the induced intra-molecular motion is subject of a long standing controversy. The molecules are excited with 400 nm pump pulses to the locally excited state (LE). We measure the intensity of several Bragg reflections as a function of the time-delay between the pump pulse and the x-ray probe pulse. The diffraction transients are modulated on a 10 ps timescale with a surprisingly large amplitude of several percent, although the excitation density is only  $10^{-4}$ . This suggests an interpretation in terms of inter-molecular dynamics, which we attribute to solvation of the excited state dipole in the polar solvent of the crystal itself. On the basis of the experimental findings we discuss the perspectives for studying ultrafast molecular processes by femtosecond x-ray diffraction.

MO 12.4 Mo 15:00 H12

**Determination of the excited state twisting angle of the chromophore of green fluorescent protein** — ●OMAR F. MOHAMMED<sup>1</sup>, ANWAR USMAN<sup>1</sup>, JIAN DONG<sup>2</sup>, KYRYL M. SOLNTSEV<sup>2</sup>, ERIK T. J. NIBBERING<sup>1</sup>, and LAREN M. TOLBERT<sup>2</sup> — <sup>1</sup>Max Born Institut für Nichtlineare Optik und Kurzzeitspektroskopie, D-12489 Berlin, Germany — <sup>2</sup>School of Chemistry and Biochemistry, Georgia Institute of Technology; Atlanta, GA, USA

Whereas in wild type green fluorescent protein (GFP), the photochemical dynamics of the chromophore consists of a Förster cycle with excited state proton transfer and a high quantum yield for fluorescent emission, the chromophore in solution, p-hydroxybenzylidene-imidazolidinone (HBDI) shows ultrafast internal conversion. We report [*J. Am. Chem. Soc.* 127, 11214 (2005)] on ultrafast polarization-sensitive infrared (IR) spectroscopy of the excited state structure of HBDI, from which we draw conclusions on the importance of twisting motions. Our focus is on the orientation of the transition moment of the IR-active carbonyl stretching

vibration of HBDI relative to that of the electronic transition dipole moment, which indicates that the C=O vibration acts as a spectator mode for the relative orientation of the phenolate and imidazolidinone groups. We have determined the anisotropy of the C=O vibration of HBDI in the S0 and S1 states for three charged configurations (anionic, neutral and cationic form). We find that our estimated value for the C=O bond vector in the S1-state can only be explained by a single twist of 120 degrees or a hula twist of 150 degrees, much larger than the twisting angle of 90 degrees found in quantum chemical calculations.

MO 12.5 Mo 15:15 H12

**Structural Evolution in the Primary Stages of Trans/Cis Isomerization of the Chromophore in Photoactive Yellow Protein** — ●KARSTEN HEYNE<sup>1,2</sup>, OMAR F. MOHAMMED<sup>1</sup>, ANWAR USMAN<sup>1</sup>, JENS DREYER<sup>1</sup>, ERIK T.J. NIBBERING<sup>1</sup>, and MICHAEL A. CUSANOVICH<sup>3</sup> — <sup>1</sup>Max Born Institut für Nichtlineare Optik und Kurzzeitspektroskopie, Max-Born Strasse 2A, 12489 Berlin, Germany — <sup>2</sup>Freie Universität Berlin, Fachbereich Physik, Arnimallee 14, 14195 Berlin, Germany — <sup>3</sup>Department of Biochemistry and Molecular Biophysics, University of Arizona, Tucson, Arizona 85721, United States of America

The primary structural evolution upon electronic excitation of photoactive yellow protein (PYP) in solution has been studied with a combined approach of polarization sensitive ultrafast infrared spectroscopy and density functional theory calculations (Heyne et al., *J. Am. Chem. Soc.*, in press). We identify the  $\nu(C_8-C_9)$  chromophore marker mode and show that upon generation of the intermediate  $I_0$  state with a 3 ps time constant a full trans/cis isomerization occurs. Anisotropy measurements of the  $\nu(C=O)$  marker mode of Glu46 show that the PYP photoisomerization involves flipping of the enone thioester linkage without significant relocation of the phenolate moiety. Comparison between experiment and theory reveal an important influence of the planarity of the chromophore on the vibrational band patterns. In particular, the chromophore in the dark P state turns out to have a trans geometry with the C=O group slightly tilted out-of-plane, in accordance with an earlier reported structure obtained in an X-ray diffraction study of PYP crystals. In contrast, the  $I_0$  state has a planar configuration.

MO 12.6 Mo 15:30 H12

**Multi-Photon Ionization of Molecular Nitrogen by Femtosecond Soft X-ray FEL Pulses** — ●MATHIAS RICHTER<sup>1</sup>, ANDREI A. SOROKIN<sup>1,2</sup>, SERGEY V. BOBASHEV<sup>2</sup>, and KAI TIEDTKE<sup>3</sup> — <sup>1</sup>Physikalisch-Technische Bundesanstalt, PTB, Abbestrasse 2-12, D-10587 Berlin, Germany — <sup>2</sup>Ioffe Physico-Technical Institute, Polytekhnicheskaya 26, 194021 St. Petersburg, Russia — <sup>3</sup>Deutsches Elektronensynchrotron, DESY, Notkestrasse 85, D-22603 Hamburg, Germany

At the new free-electron laser (FEL) for vacuum ultraviolet (VUV) and soft X-ray radiation of the Deutsches Elektronensynchrotron (DESY) in Hamburg, multi-photon double ionization of molecular nitrogen was observed and studied by ion time-of-flight spectroscopy. The experiments were performed at the microfocus beamline BL2 of the VUV-FEL with photon pulses of estimated 25-fs duration and irradiance levels up to 20 Terrawatt per square centimeter at a photon energy of 38 eV. Emphasis was laid on the determination of absolute photon numbers per pulse with the help of a calibrated setup which allows the investigation of non-linear effects by quantitative measurements. Results are discussed in terms of a sequential double photoionization scheme.

MO 12.7 Mo 15:45 H12

**A new method for molecule imaging** — ●TEODORA BAEVA — Institut für theoretische Physik I, Universität Düsseldorf, Germany

Imaging of molecules with sub-angstrom precision and sub-femtosecond resolution is one of the hottest topics in the field of molecule physics at the moment. Two basic methods attract attention: imaging by means of high-harmonics generated by the molecule in a laser field and imaging by means of rescattered electrons, which are ionised by the field and driven back to recollide.

We present a new method for molecule imaging based on the molecule interaction with a single attosecond pulse. We also introduce a new procedure for the effective generation of such pulses by means of laser-overdense plasma interaction and tools for their manipulation.

## MO 13 Molecular Clusters I

Zeit: Montag 14:00–16:00

Raum: H10

MO 13.1 Mo 14:00 H10

**Innershell excitation of free nano particles** — ●B. LANGER<sup>1,2</sup>, H. BRESCH<sup>1</sup>, R. LEWINSKI<sup>1</sup>, P. BRENNER<sup>1</sup>, R. FLESCH<sup>1</sup>, C. GRAF<sup>1</sup>, T. MARTCHENKO<sup>3</sup>, O. GHAFUR<sup>3</sup>, M. J. J. VRAKING<sup>3</sup>, and E. RÜHL<sup>1</sup> — <sup>1</sup>Institut für Physikalische Chemie I, Universität Würzburg, Am Hubland, 97074 Würzburg — <sup>2</sup>Max-Born-Institut für Nichtlineare Optik und Kurzzeitspektroskopie, Max-Born-Straße 2A, 12489 Berlin — <sup>3</sup>FOM Institute AMOLF, Amsterdam, The Netherlands

We have studied inner shell excitations in free nano particles using synchrotron radiation. Our particles were transferred into the gas phase by an aerosol generator. An additional differential mobilisation analyser (DMA) made it possible to generate a continuous beam of size selected nano particles that was focussed into the vacuum chamber by an aerodynamical lens. This approach allowed us to prepare free nano particles which were produced by colloidal chemistry. We have measured the total electron yield to characterise the electronic structure of nano particles in the region of their inner shell excitations.

First experiments were performed on size selected NaCl nano particles (radius = 50–175 nm) in the region of the Cl 2*p* and the Na 1*s* excitation. Measurements in the region around the O 1*s* absorption threshold show that these particles contain only little water. In contrast, nanoscopic salt particles (Na<sub>2</sub>SO<sub>4</sub>·10 H<sub>2</sub>O) that contain chemically combined water show a significant absorption in this region which might be of interest to study the binding structure of such water. In addition, we have studied the influence of coatings to the electronic structure of free core-shell particles. Here we used ZnS particles (radius = 60 nm) with a 5 nm SiO<sub>2</sub> shell.

MO 13.2 Mo 14:15 H10

**Photoelectron spectroscopy of strontium cluster anions** — ●OLEG KOSTKO<sup>1</sup>, ORI CHESHNOVSKY<sup>2</sup>, and BERND V. ISSENDORFF<sup>1</sup> — <sup>1</sup>Fakultät für Physik, Universität Freiburg, Stefan-Meier-Str. 21, 79104 Freiburg — <sup>2</sup>School of Chemistry, The Raymond and Beverly Sackler Faculty of Sciences, Tel Aviv University, 69978 Tel Aviv, Israel

Size-selected strontium cluster anions with a temperature of T=100K have been studied by photoelectron spectroscopy. The spectra exhibit clear structures which in combination with ab initio DFT calculations can be used to identify the geometry of the clusters. Comparison of the photoelectron spectra with the spectra of other divalent metals such as magnesium and zinc shows clear distinctions. All of them exhibit a band gap for small sizes. But the photoelectron spectra of larger Mg and Zn clusters reveal free electron-like density of states, whereas in the case of Sr clusters an electron shell structure is not visible. This is the result of strong hybridization of the 5*s* band with the empty 4*d* band (instead of *s-p* hybridization like in Mg and Zn clusters), which perturbs the electron shell structure and leads to a high DOS at E<sub>F</sub> even for smaller clusters.

MO 13.3 Mo 14:30 H10

**Winkelaufgelöste Photoelektronenspektroskopie an Natrium-Clustern** — ●CHRISTOF BARTELS, CHRISTIAN HOCK, JÖRG SCHWÖBEL, RAPHAEL KUHNEN, ABDOLLAH MALAKZADEH, PASCAL DIDIER und BERND VON ISSENDORFF — Institut für Physik, Universität Freiburg, Stefan-Meier-Straße 19, 79104 Freiburg

Ein Bildspektrometer zur Messung von winkelaufgelösten Photoelektronenspektren an Clustern wurde aufgebaut. Erste Messungen mit ns-Laserpulsen (XeCl-Excimerlaser, 4,02 eV Photonenenergie) an negativen Natrium-Clusterionen wurden durchgeführt.

Die früher an Natrium gemessenen klassischen (energieauflösenden) Photoelektronenspektren [1] lassen sich im Rahmen des Jelliummodells erklären. Dieses Modell sagt für Photoelektronen aus Zuständen mit verschiedenen Drehimpulsquantenzahlen unterschiedliche Winkelverteilungen voraus.

Die Messungen an kleinen Na<sub>n</sub><sup>-</sup>-Clustern (*n* = 13, 19, 20, 39) zeigen jedoch stets eine Anisotropie mit Emissionsmaxima entlang der Polarisationsachse des Laserlichts, unabhängig vom Elektronendrehimpuls. Diese Verteilung ist charakteristisch für die Emission von *s*-Elektronen und könnte so gedeutet werden, dass sich hier der Drehimpuls des Valenzelektrons eines Na-Atoms bemerkbar macht und nicht der Drehimpuls der Elektronen im Rahmen des Jelliummodells. Große Cluster (114, ..., 355) jedoch zeigen isotrope Elektronenverteilungen.

[1] Wrigge et al., Phys. Rev. A 65, 063201 (2002)

MO 13.4 Mo 14:45 H10

**Gas Phase Vibrational Spectroscopy of Bimetallic Oxide Cluster Anions** — ●E. JANSSENS<sup>1,2</sup>, G. SANTAMBROGIO<sup>1</sup>, M. BRÜMMER<sup>1</sup>, L. WÖSTE<sup>1</sup>, P. LIEVENS<sup>2</sup>, J. SAUER<sup>3</sup>, G. MEIJER<sup>4</sup>, and K.R. ASMIS<sup>4</sup> — <sup>1</sup>Institut für Experimentalphysik, F.U. Berlin, Arnimallee 14, 14195 Berlin — <sup>2</sup>Laboratorium voor Vaste-Stoffysica en Magnetisme, K.U. Leuven, Celestijnenlaan 200 D, 3001 Leuven, Belgium — <sup>3</sup>Institut für Chemie, H.U. Berlin, Unter den Linden 6, 10099 Berlin — <sup>4</sup>Fritz-Haber Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin

Transition metal oxides on oxide surfaces play a central role in heterogeneous catalysis. However because of the complex interactions between the active sites and the support, the catalytic mechanisms are not completely known. Molecular beam studies on mass-selected particles under well controlled conditions can aid to understand these interesting systems. Here, we present the first systematic infrared study of bimetallic oxide clusters in the gas phase.

Mixed V<sub>n</sub>Ti<sub>m</sub>O<sub>p</sub><sup>-</sup> clusters are studied with IR multiphoton dissociation spectroscopy in the 500 to 1200 cm<sup>-1</sup> range and assigned on the basis of harmonic frequencies calculated with DFT. The clusters are produced in a dual laser vaporization source, stored in an ion trap, and irradiated with IR light of a free electron laser. The closed shell (V<sub>2</sub>O<sub>5</sub>)<sub>n-1</sub>(VTiO<sub>5</sub>)<sup>-</sup> (*n* = 2–4) clusters are shown to form caged structures similar to their iso-electronic monometallic counterparts, the neutral vanadium oxide clusters (V<sub>2</sub>O<sub>5</sub>)<sub>n</sub> (*n* = 2–4). Titanium-richer anions, V<sub>4-n</sub>Ti<sub>n</sub>O<sub>10</sub><sup>-</sup> (*n* = 1–4), prefer to maintain the tetrahedral shape of V<sub>4</sub>O<sub>10</sub> rather than pairing electrons, leading to a quartet ground state in Ti<sub>4</sub>O<sub>10</sub><sup>-</sup>.

MO 13.5 Mo 15:00 H10

**Pump-Probe-Photoelectron-Spectroscopy of C<sub>60</sub><sup>-</sup>** — ●CHRISTINE WEHRSTEIN, RAPHAEL KUHNEN, ABDOLLAH MALAKZADEH, PASCAL DIDIER, and BERND V. ISSENDORFF — Physikalisches Institut, Universität Freiburg, Stefan-Meier-Str. 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 relaxation processes in a highly correlated many-electron systems.

C<sub>60</sub><sup>-</sup> clusters have been studied by femtosecond laser photoelectron spectroscopy, measuring intensity dependencies for single pulse excitation with 266nm, 400nm and 800nm light as well as two colour pump-probe spectra. In the single pulse spectra structures are observed which can be identified as resonant multiphoton detachment of C<sub>60</sub><sup>-</sup>. The corresponding intermediate excited states exhibit strongly different decay times.

MO 13.6 Mo 15:15 H10

**Electron-Ion-Coincidence Study of C<sub>60</sub> Fragmentation** — ●SANJA KORICA, AXEL REINKÖSTER, JENS VIEFHAUS, DANIEL ROLLES, REINER HENTGES, MARKUS BRAUNE, and UWE BECKER — Fritz-Haber-Institut der MPG, Faradayweg 4-6, Berlin, Germany

In order to get a deeper insight in the valence shell photofragmentation dynamics of C<sub>60</sub> we have performed photoelectron-photoion coincidence measurements (PEPICO) in this energy region. Our results are supported with the previous non-coincident electron and ion measurements. The measurements were performed at the BW3 beamline of HASYLAB. C<sub>60</sub> molecules in the gas phase were ionized by the monochromatic synchrotron radiation and the outgoing electrons and ions were detected with the time-of-flight analysers located opposite to each other. Our results show that the most intense coincidences are between electron and C<sub>60</sub><sup>(q+)</sup> ions (q=1-3), but also coincidences with the C<sub>60-2m</sub><sup>(2+)</sup> ions are clearly discernible. Possible mechanisms for these fragmentation events will be discussed.

MO 13.7 Mo 15:30 H10

**Ionisation von C<sub>60</sub> in intensiven Laserfeldern** — ●A. BECKER<sup>1</sup>, A. JARON-BECKER<sup>2</sup> und F.H.M. FAISAL<sup>3</sup> — <sup>1</sup>Max-Planck-Institut für Physik komplexer Systeme, Nöthnitzer Str. 38, 01187 Dresden — <sup>2</sup>Institut für Physikalische Chemie und Elektrochemie, Technische Universität Dresden, 01062 Dresden — <sup>3</sup>Fakultät für Physik, Universität Bielefeld, 33501 Bielefeld

Wir haben die Ionisation von Fullerenen in intensiven Laserfeldern theoretisch untersucht. Dazu haben wir einen *S*-Matrix-Ansatz für Atome in starken Feldern <sup>1</sup> auf Fullerene erweitert, indem wir die struk-

turellen Aspekte des Moleküls, wie Radius und Molekülwellenfunktion, berücksichtigt haben. Die Ergebnisse für die Sättigungsintensitäten von  $C_{60}$  sind in sehr guter Übereinstimmung mit experimentellen Daten<sup>2</sup>. Unsere Analyse der Daten zeigt den Einfluß von Interferenzeffekten auf die laserinduzierte Ionisationsdynamik eines Fullerenes.

<sup>1</sup> A. Becker and F.H.M. Faisal, *J. Phys. B* **38**, R1 (2005).

<sup>2</sup> V.R. Bhardwaj, P.B. Corkum and D.M. Rajner, *Phys. Rev. Lett.* **91**, 203004 (2003).

MO 13.8 Mo 15:45 H10

**Ionisationspotentiale von molekularen Diamanten (diamondoids)** — ●KONSTANTIN LENZKE<sup>1</sup>, CHRISTOPH BOSTEDT<sup>1</sup>, MATTHIAS HOENER<sup>1</sup>, HEIKO THOMAS<sup>1</sup>, THOMAS MÖLLER<sup>1</sup>, JEREMY E. DAHL<sup>2</sup>, S. G. LIU<sup>2</sup> und R. M. K. CARLSSON<sup>2</sup> — <sup>1</sup>Technische Universität Berlin, PN 3-1, Hardenbergstr. 36, 10623 Berlin, Germany — <sup>2</sup>Molecular Diamond Technologies, Chevron, P.O. Box 1627, Richmond, California 94802, USA

## MO 14 Ultrafast IR and Raman Probe and Control

Zeit: Montag 16:30–18:30

Raum: H12

MO 14.1 Mo 16:30 H12

**Bulk ice at room temperature** — ●MARCUS SCHMEISSER, HRISTO IGLEV, and ALFRED LAUBEREAU — Technische Universität München, Physik-Department E11, James-Franck-Straße, 85748 Garching

The complex three-dimensional hydrogen-bonded network of water molecules gives rise to unusual solid and liquid properties and strongly affects the melting behaviour of ice. Here we present the first experimental evidence for ultrafast superheating of bulk ice using an ultrafast temperature-jump technique with subpicosecond pulses for excitation and probing in the mid-infrared. The hydroxilic stretching vibrations (OH or OD) of isotopically mixed ice are used for energy deposition and for the fast and sensitive spectral probing of local temperature and H-bonding environment.

Measurements performed for a HDO:D<sub>2</sub>O specimen with initial temperature of 270 K (close to the melting point of 274.8 K) provide evidence for substantial superheating of the ice lattice up to 301±2 K that persists over the monitored time interval of 250 ps without melting [1, 2]. For higher pumping levels evidence for ultrafast melting of bulk ice is obtained [1].

[1] H. Iglev, M. Schmeisser, K. Simeonidis, A. Thaller und A. Laubereau, *Nature* (2006), in press.

[2] H. Iglev, M. Schmeisser, A. Thaller und A. Laubereau, *subm.*

MO 14.2 Mo 16:45 H12

**Ultrafast vibrational relaxation of the O–H bending mode in liquid H<sub>2</sub>O** — ●SATOSHI ASHIHARA, NILS HUSE, ERIK T. J. NIBBERING, and THOMAS ELSAESSER — Max-Born-Institut für Nichtlineare Optik und Kurzzeitspektroskopie, Max-Born-Str. 2A, D-12489 Berlin, Germany

The mechanisms of vibrational energy transfer in liquid water are essential for the understanding of its physical and chemical properties. The dynamics of the O–H stretching vibrations in water have been intensively studied in recent years but much less is known about the dynamics of the O–H bending mode. This mode is highly relevant for the geometry of the intermolecular hydrogen bonds and for the relaxation of O–H stretching excitations. Here we study the population relaxation of the O–H bending mode in pure liquid H<sub>2</sub>O in mid-infrared pump-probe experiments with 100 fs time resolution [1]. After resonant excitation of the  $v = 0$  to 1 bending transition, a  $v = 1$  lifetime of 170 fs is measured. This short lifetime is determined by the anharmonic couplings to the fluctuating liquid environment forming an extended hydrogen bond network. The population relaxation is followed by slower spectral diffusion and energy redistribution processes within 1-2 ps. Femtosecond excitation also induces ultrafast nonlinear changes of the broad librational absorption occurring at frequencies below the  $v = 0$  to 1 bending transition.

[1] N. Huse, S. Ashihara, E.T.J. Nibbering, T. Elsaesser, *Chem. Phys. Lett.* **404** (2005) 389.

MO 14.3 Mo 17:00 H12

**A picosecond thermometer and pressure gauge for H-bonded systems** — ●MARCUS SCHMEISSER, HRISTO IGLEV, and ALFRED LAUBEREAU — Technische Universität München, Physik-Department E11, James-Franck-Straße, 85748 Garching

Diamondoids sind ideale Diamantcluster am molekularen Limit. Das erste Diamondoid Adamantane besteht aus dem kleinsten zusammenhängenden Käfig im Diamantgitter, alle anderen werden durch Hinzufügen weiterer Käfige gebildet. Cluster können größen- und sogar struktursepariert werden und sind daher ideale Systeme um grundlegende Fragen der Clusterphysik zu untersuchen.

Wir haben die Ionisationspotentiale der ersten Diamondoids von Adamantane (ein Käfig) bis Pentamantane (fünf Käfige) aus Absorptionsspektren im Bereich von 100 bis 200 nm bestimmt. Die Untersuchungen wurden am Strahlrohr I des HasyLab (DESY) in der Gasphase durchgeführt. Die erzeugten Ionen wurden mit einem Flugzeit - Massenspektrometer (TOF) analysiert und Ionenausbeutespektren aufgenommen. Die Ionisationspotentiale skalieren mit der Clustergröße, es zeigen sich aber auch interessante Zusammenhänge zwischen den Ionisationspotentialen und Clusterstrukturen. Die Ergebnisse werden mit aktuellen theoretischen Vorhersagen verglichen und diskutiert.

A spectroscopic method for sensitive temperature and pressure measurements in hydrogen-bonded materials on a picosecond timescale is demonstrated [1, 2]. The method is verified for an isotopic mixture of ice at 200 K and ambient pressure using the OH- and OD-stretching vibrations for ultrafast heating of the sample. The same vibration modes are known to be sensitive probes for H-bonding and represent suitable tools to distinguish local ice or water components with a time resolution of a few picoseconds.

We calibrate our picosecond thermometer taking into account the isochoric character of the ultrafast temperature rise in the sample, i.e the simultaneous pressure increase because of the slow volume expansion (on the nanosecond timescale). We observe a temperature rise up to 20±2 K with a simultaneous pressure increase up to 26±4 MPa. Including the pressure-induced spectral changes in the data analysis we were able to extract the temporal evolution of the temperature and pressure changes in the sample. Our investigation shows that the use of a temperature scale is meaningful for ice as early as 25 ps after energy deposition [2].

[1] H. Iglev, M. Schmeisser, K. Simeonidis, A. Thaller und A. Laubereau, *Nature* (2006), in press.

[2] H. Iglev, M. Schmeisser, A. Thaller und A. Laubereau, *subm.*

MO 14.4 Mo 17:15 H12

**Liquid phase interactions studied with time resolved hyper-Rayleigh scattering** — ●TIAGO BUCKUP<sup>1</sup>, MARCUS MOTZKUS<sup>1</sup>, RICARDO CORREIA<sup>2</sup>, JÚLIO SCHOFFEN<sup>2</sup>, and SILVIO CUNHA<sup>2</sup> — <sup>1</sup>Physikalische Chemie, Phillips Universität Marburg, 35043 Marburg, Germany — <sup>2</sup>Instituto de Física, UFRGS, Porto Alegre, Brazil

The liquid phase is well-known for its local order, where orientation and position correlations between molecules only prevail for several nanometers and where the corresponding interactions happen at different timescales. Due to the difficulties of studying the superposition of many-body interactions in the liquid phase, there is a high demand for new techniques which provide additional information about these complex interactions. This work introduces the concept of time resolved hyper-Rayleigh scattering with femtosecond resolution (TRHRS). TRHRS is based on the generation of elastic incoherent second harmonic radiation, a process related to the first molecular hyperpolarizability  $\beta$ . The obtained relaxation behavior for two model liquids (carbon tetrachloride and acetonitrile) agrees consistently with those obtained from spectral domain techniques. TRHRS opens the possibility not just to detect the long wings hardly seen in scattering spectra, but also to investigate the interactions in biological systems with high spatial and temporal resolution and to act as a new probe for orientation control experiments.

MO 14.5 Mo 17:30 H12

**Small Bandwidth 400 nm Pulses for Femtosecond Stimulated Raman Spectroscopy** — ●HILMAR SCHACHENMAYR, PETER GILCH, and STEFAN LAIMGRUBER — Department für Physik, Ludwig-Maximilians-Universität, Oettingenstr. 67, D-80538 München, Germany

Femtosecond Stimulated Raman Spectroscopy (FSRS) copes with several drawbacks of conventional time resolved Raman spectroscopy, as

there are weak signal levels, strong fluorescence backgrounds, and an *instrumental* time bandwidth limit. Thereby, FSRS renders Raman techniques competitive with time resolved IR spectroscopy for monitoring fast molecular re-arrangements. In FSRS spectroscopy a femtosecond white light pulse and an intense laser pulse (Raman pump) cross in the sample. The white light spectrum gets modulated and the modulations can be transformed into the Raman spectrum of the sample. In most applications a spectrally narrowed TiSa pulse at 800 nm serves as Raman pump. For many photo-active molecules absorbing in the UV a 400 nm Raman pump is advantageous due to substantial resonance enhancements. We here report on a set-up generating 400 nm pulses for FSRS. Two equally but oppositely in sign chirped 800 nm pulses are mixed in a non-linear crystal. This results in intense small bandwidth 400 nm pulses. With these pulses FSRS spectra with high signal levels and good spectral resolution can be obtained. Examples for their application will be given.

MO 14.6 Mo 17:45 H12

**Ultrafast Dynamics of Molecules Exhibiting Double Minimum Potential** — ●A.V. SCARIA, J. KONRADI, A.K. SINGH, and A. MATERNY — International University Bremen, Germany

Femtosecond time-resolved four-wave mixing (FWM) spectroscopy is a powerful technique for observing ultrafast molecular dynamics. Studies are carried out on molecules exhibiting double minimum potential structure in gas phase and in liquid phase using different FWM techniques. Of particular interest among them are *e.g.* molecules showing ring puckering vibrations (characteristic for cyclic molecules having -CH<sub>2</sub>-, -O- or -S- groups). Ring puckering vibrations involve the bending motions of the group out of the plane of the ring. The potential energy curve for the vibration shows, therefore, two (nearly) identical minima corresponding to the ring being puckered upwards or downwards. Investigations are carried out on Trimethylene Sulfide (TMS) and Trimethylene Oxide (TMO) having barrier heights of 274 and 15 cm<sup>-1</sup>, respectively. The time-resolved techniques applied are femtosecond degenerate four-wave mixing (DFWM) and coherent anti-Stokes Raman scattering (CARS). The observed dynamics of these vibrational modes obtained from gas and liquid phase will be presented and discussed in comparison with each other.

MO 14.7 Mo 18:00 H12

**Kontrolle der Produktausbeuten der Photofragmentation von Deuteriumchlorid-Ionen (DCI<sup>+</sup>): Cl + D<sup>+</sup> ← DCI<sup>+</sup> → Cl<sup>+</sup> + D** — ●H. GEORG BREUNIG<sup>1</sup>, ALEXANDRA LAUER<sup>1</sup>, MIKHAIL V. KOROLKOV<sup>1,2</sup> und KARL-MICHAEL WEITZEL<sup>1</sup> — <sup>1</sup>Philipps Universität Marburg, Fachbereich Chemie, 35032 Marburg, Germany — <sup>2</sup>Stephanov Institute of Physics, National Academy of Science, 220602 Minsk, Republic of Belarus

Wir untersuchen die Kontrolle der Photofragmentation von Deuteriumchlorid-Ionen (DCI<sup>+</sup>) durch ultrakurze IR-Laserpulse in Experimenten und anhand der numerischen Lösung gekoppelter Schrödinger-Gleichungen. Die Berechnungen zeigen, dass das Ionen-Ausbeuteverhältnis von Cl<sup>+</sup> zu D<sup>+</sup> durch eine geeignete Wahl von Laserpulsparametern, insbesondere der Zentralwellenlänge, der Pulsdauer, der Intensität und dem Chirp manipuliert werden kann [1]. Die Untersuchung der zeitabhängigen Besetzungen zeigt phasensensitive, miteinander konkurrierende Anregungen innerhalb und zwischen elektronischen Zuständen.

Zusätzlich haben wir Ein- und Zweifarb-Experimente zur Dissoziation von DCI<sup>+</sup>-Ionen bei 800 nm [2] und im Bereich 3.5 μm bis 7.5 μm (2857 cm<sup>-1</sup> bis 1333 cm<sup>-1</sup>) durchgeführt. Insbesondere zeigen wir, dass das Verhältnis der Produktausbeute D<sup>+</sup>/Cl<sup>+</sup> durch den Chirp der Laserpulse im mittleren IR-Bereich kontrolliert werden kann.

[1] M.V. Korolkov, K.-M. Weitzel, J. Chem. Phys. 123, 164308, (2005)

[2] H.G. Breunig, A. Lauer, K.-M. Weitzel, Proceedings of the Femtochemistry VII (2005)

MO 14.8 Mo 18:15 H12

**Local control of molecular fragmentation: the role of orientation** — ●PHILIPP MARQUETAND<sup>1</sup>, CHRISTOPH MEIER<sup>2</sup>, and VOLKER ENGEL<sup>1</sup> — <sup>1</sup>Institut für Physikalische Chemie, Am Hubland, 97074 Würzburg, Germany — <sup>2</sup>Laboratoire Collisions, Agrégats et Réactivité, IRSAMC,\*Université Paul Sabatier,\*31062 Toulouse, France

Local control theory, where the instantaneous response of a system to an external field determines the control field, is employed for the purpose to induce molecular fragmentation processes via infrared (IR) excitation. In particular, the effects of the orientational motion are investigated and compared to the idealized case of a frozen rotation. It is shown that the rotational degree of freedom is crucial for the applicability of the employed local control algorithm. The addition of an additional static electric field which induces a molecular preorientation, offers an efficient way for the local control. In particular, with increasing static field strength, the fragmentation yield approaches unity so that the idealized rotation-less case is recovered. Numerical results are presented for the NaI molecule.

## MO 15 Molecular Clusters II

Zeit: Montag 16:30–18:45

Raum: H10

MO 15.1 Mo 16:30 H10

**Effiziente globale Optimierung: Von Clusterstrukturen bis zur Proteinfaltung** — ●BERND HARTKE — Institut für Physikalische Chemie, Christian-Albrechts-Universität, Olshausenstr. 40, 24098 Kiel

Mit stochastisch-heuristischen globalen Optimierungsmethoden [1,2] konnten wir unvoreingenommene Strukturvorschläge für Solvationscluster der Alkali-Kationen machen [3]. Simulationen der IR-Spektren der besten Strukturen stimmen hervorragend mit experimentellen Spektren überein [4] und werden von MD-Simulationen bei experimentell relevanten Temperaturen bis 150 K gestützt. Daraus ergibt sich eine neue Hypothese zur Begründung magischer Zahlen in diesen Systemen [5].

Kürzlich konnten wir unsere Methoden auch auf das verwandte Problem der Proteinfaltung ausdehnen [6]. In ersten Anwendungen konnten wir nicht nur Testsysteme, sondern auch reale Proteine aus der Proteindatenbank PDB erfolgreich falten.

[1] B. Hartke, J. Comput. Chem. 20 (1999) 1752.

[2] B. Hartke, Angew. Chem. 114 (2002) 1534.

[3] F. Schulz und B. Hartke, Chem. Phys. Chem. 3 (2002) 98.

[4] F. Schulz, B. Hartke und J. Lisy, Manuskript in Vorbereitung.

[5] F. Schulz und B. Hartke, Theor. Chem. Acc. 114 (2005) 357.

[6] F. Koskowski und B. Hartke, J. Comput. Chem. 26 (2005) 1169.

MO 15.2 Mo 16:45 H10

**Spektroskopie an kleinen Wasser-Clustern mit Synchrotronstrahlung** — ●SILKO BARTH<sup>1</sup>, VOLKER ULRICH<sup>1</sup>, SANJEEV JOSHI<sup>1</sup>, AXEL REINKÖSTER<sup>2</sup> und UWE HERGENHAHN<sup>1</sup> — <sup>1</sup>Max-Planck-Institut für Plasmaphysik, EURATOM Assoziation, Boltzmannstr. 2, 85748 Garching — <sup>2</sup>Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin

Wir haben die Ionenausbeute von kleinen Wasser-Clustern entlang der Sauerstoff-K-Kante mit Flugzeit-Massenspektroskopie bestimmt. Unsere Ergebnisse können mit Absorptions-Messungen an flüssigem Wasser und an Eis verglichen werden. Die Messungen an flüssigem Wasser wurden in einer neueren, viel diskutierten Arbeit als Hinweis auf eine drei- statt vierfache Koordination der Wassermoleküle in der Flüssigkeit interpretiert [1]. Unsere Spektren zeigen eine Mischung der Charakteristika von flüssigem Wasser und Volumen-Eis.

Wir haben weiterhin das erste Ionisationspotential von (H<sub>2</sub>O)<sub>N</sub> mit N = 2...5 bestimmt.

[1] Ph. Wernet *et al.*, Science 304, 995 (2004).

MO 15.3 Mo 17:00 H10

**Spectroscopic Characterization of Proton Wires: IR Spectra of Microsolvated Protonated Ethanol Chains** — ●OTTO DOPFER and NICOLA SOLCA — Institut für Physikalische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

Proton transfer, proton transport, and proton pumps are fundamental chemical and biological phenomena. Detailed understanding of these processes at the molecular level requires knowledge of the potential energy surface describing the proton wire. Mass spectrometric, spectroscopic, and quantum chemical characterization of proton-bound complexes under isolated or controlled microsolvation conditions provide the most direct access to this potential, yielding valuable information on the mobility of excess protons in solution. The present work reports IR photodissociation spectra [1] of size-selected protonated ethanol complexes of the type (EtOH) $m$ H $^+$ -Ln, with L=Ar and N<sub>2</sub>, m=1-4, and n=0-5. The IR spectra provide detailed information on the degree of delocalization of the excess proton along the ethanol chain as a function of the length of the chain (m), the type of solvent (L), and the degree of solvation (n) [2,3]. Significantly, the symmetry of the proton bridge (Zundel or Eigen type) is found to depend sensitively on the symmetry of the microsolvation environment. Moreover, the acidity of the terminal OH groups decreases with the length of the chain. Density functional calculations support the interpretation derived from the spectroscopic data.

[1] O. Dopfer, *Int. Rev. Phys. Chem.* 22, 437 (2003). [2] N. Solca and O. Dopfer, *J. Am. Chem. Soc.* 126, 9520 (2004). [3] N. Solca and O. Dopfer, *J. Phys. Chem. A* 109, 6147 (2005).

MO 15.4 Mo 17:15 H10

**Excited state hydrogen transfer in aminopyridine dimer: details of the reaction coordinate** — ●THOMAS SCHULTZ, HANS-HERMANN RITZE, ELENA SAMOYLOVA, VALORIS REID SMITH, INGOLF VOLKER HERTEL, and WOLFGANG RADLOFF — Max Born Institut, Max Born Str. 2A, 12489 Berlin, Germany

The doubly hydrogen-bonded aminopyridine dimer (APd) resembles a Watson-Crick base pair and served as model system for a theoretically predicted hydrogen-transfer process in the excited state. We characterized this reaction experimentally by femtosecond pump-probe ionization spectroscopy. The reaction rate ( $1.2\text{--}1.8 \times 10^{10} \text{ s}^{-1}$ ) varied non-monotonously with the excitation energy and showed a considerable H/D isotope effect. Based on our observations and ab initio calculations, we propose an excited state reaction pathway with a rate determining barrier for the H-transfer. The cluster structure appears to be a crucial factor determining the occurrence and rate of the H-transfer reaction. This may explain why the corresponding reaction was not observed for the adenine-thymine base pair, which adopts a non-Watson-Crick structure in the gas phase.

MO 15.5 Mo 17:30 H10

**Mass-selected Gas Phase Infrared Spectroscopy of NH<sub>4</sub><sup>+</sup>(NH<sub>3</sub>)<sub>n</sub> (n=0-7)** — ●GABRIELE SANTAMBROGIO<sup>1</sup>, MATHIAS BRÜMMER<sup>1</sup>, SARA FONTANELLA<sup>1</sup>, YONGGANG YANG<sup>2</sup>, OLIVER KÜHN<sup>2</sup>, and KNUT R. ASMIS<sup>3</sup> — <sup>1</sup>Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany — <sup>2</sup>Institut für Chemie und Biochemie, Freie Universität Berlin, Takustr. 3, 14195 Berlin, Germany — <sup>3</sup>Fritz-Haber-Institut der Max-Planck-Gesellschaft, Abteilung Molekülphysik, Faradayweg 4-6, 14195 Berlin, Germany

The hydrogen bond interaction is key in understanding the structure and properties of water and biomolecules. However, our understanding of strong, low-barrier hydrogen bonds and their central role in enzyme catalysis, biomolecular recognition, proton transfer across biomembranes and proton transport in aqueous media remains sketchy.

Here we present results on the infrared photodissociation spectroscopy of gas phase mass selected NH<sub>4</sub><sup>+</sup>(NH<sub>3</sub>)<sub>n</sub> (n=0-7) in the region between 600 and 2000 cm<sup>-1</sup>. The ammonia umbrella mode is observed at 1300 cm<sup>-1</sup> for n=1 and is monotonically red-shifted down to 1100 cm<sup>-1</sup> for n=7. Its position is a measure for the strength of the hydrogen bonds and shows evidence for closing of the first solvation shell after n=4. The threefold degenerate antisymmetric stretch mode of the ammonium ion is observed around 1500 cm<sup>-1</sup>. Its degeneracy is lifted upon solvation until a symmetric solvation shell is reached for n=4. Only the n=1 cluster is predicted to exhibit strong hydrogen bonding and evidence or a shared proton mode is found at 750 cm<sup>-1</sup> for n=1. Surprisingly, we also find such spectral signatures for some of the larger cluster ions.

MO 15.6 Mo 17:45 H10

**IR spectrum of the ethyl cation: nonclassical versus classical structure** — ●HORIA-SORIN ANDREI, HANNES KUCHELMEISTER, NICOLA SOLCA, and OTTO DOPFER — Institut für Physikalische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

The competition between classical and nonclassical geometries is a fundamental issue for hydrocarbon molecules. The ethyl cation (C<sub>2</sub>H<sub>5</sub><sup>+</sup>, protonated ethen) 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 and N<sub>2</sub>. 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, leaving C<sub>2</sub>H<sub>5</sub><sup>+</sup> in the most stable nonclassical geometry, the stronger interaction with N<sub>2</sub> induces a switch from a nonclassical to a classical C<sub>2</sub>H<sub>5</sub><sup>+</sup> 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).

MO 15.7 Mo 18:00 H10

**Das Phenanthren-Anion und seine Wassercluster** — ●MARTIN TSCHURL, STEFAN GILB und ULRICH BOESL — Department Chemie der TU München, Physikalische Chemie I

Die Elektronenaffinität (EA) ist eine der fundamentalen thermodynamischen Größen eines Moleküls. Sie spielt z.B. eine wichtige Rolle bei Reduktionsprozessen und beim Elektrontransfer.

Die Photodetachment-Photoelektronenspektroskopie [1] ist eine der Methoden, mit denen sich die Elektronenaffinität sehr genau bestimmen lässt.

Das Ausbleiben von Phenanthren-Anionen im Massenspektrometer stellt ein Indiz für eine negative oder sehr geringe EA des Moleküls dar. Durch stufenweise Anlagerung von Wassermolekülen und eine von Schiedt et al. [2] eingeführte Extrapolationsmethode erhärtet sich dieser Verdacht. Zusätzlich kann hier etwas über das Solvatationsverhalten von Anionen gelernt werden. Der Vergleich zwischen theoretischen Berechnungen und Messergebnissen untermauert getroffene Annahmen. Zuletzt wird noch der Brückenschlag zwischen der EA und dem Reduktionspotential der Moleküle gewagt.

[1] U. Boesl, W.J. Knott, *Mass. Spec. Rev.* 67 (1989) 171.

[2] J. Schiedt, W.J. Knott, K. Le Barbu, E.W. Schlag, R. Weinkauff, *J. Chem. Phys.* 113 (2000) 9470.

MO 15.8 Mo 18:15 H10

**Electronic excitation in the benzonitrile dimer: The intermolecular structure of the benzonitrile dimer in the S<sub>0</sub> and S<sub>1</sub> state determined by rotationally resolved electronic spectroscopy.** — ●MARCEL BÖHM<sup>1</sup>, MICHAEL SCHMITT<sup>1</sup>, CHRISTIAN RATZER<sup>1</sup>, DANIEL KRÜGLER<sup>1</sup>, KARL KLEINERMANN<sup>1</sup>, and LEO MEERTS<sup>2</sup> — <sup>1</sup>Institut für Physikalische Chemie, Universitätsstr. 26.43.02, D-40225 Düsseldorf, Germany — <sup>2</sup>Molecular- and Biophysics Group, Institute for Molecules and Materials, Radboud University Nijmegen, P.O. Box 9010, NL-6500 GL Nijmegen, The Netherlands

The benzonitrile dimer is an interesting example for a homo dimer. The rotationally resolved UV spectra of the electronic origin of the benzonitrile dimer has been measured. The benzonitrile dimer was found to be of C<sub>2h</sub> symmetry in the S<sub>0</sub> and S<sub>1</sub> state. From the inertial parameters, the N...H-distance was found to be 236 pm in the electronic ground state and 232 pm in the electronic excited state.

MO 15.9 Mo 18:30 H10

**IR and UV spectra of the gas-phase benzene dimer** — ●UNDINE ERLEKAM, MARCIN FRANKOWSKI, GERT VON HELDEN, and GERARD MEIJER — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin

The benzene dimer is a simple prototype system to get insight into dispersive interactions between aromatic molecules.

We investigate the benzene dimer via two-colour Resonance Enhanced Multi Photon Ionization (REMPI) and mass-selective Infrared (IR) ion dip spectroscopy in the C-H-stretch region. Benzene clusters are formed and internally cooled in a supersonic jet expansion. A few ns before UV excitation and ionization, the molecular beam is interrogated by a tunable IR laser. If the IR photons are resonant with a vibration in the complex, population is transferred into a vibrationally excited state, leading to a reduction of the ion signal. By recording the ion yield while tuning the IR wavelength, the IR spectrum is obtained.

UV and IR spectra of (C<sub>6</sub>H<sub>6</sub>), (C<sub>6</sub>H<sub>6</sub>)<sub>2</sub> and (C<sub>6</sub>H<sub>6</sub>)(C<sub>6</sub>D<sub>6</sub>) will be presented. (C<sub>6</sub>H<sub>6</sub>)(C<sub>6</sub>D<sub>6</sub>) forms two isomers having different UV excitation as well as IR spectra. Surprisingly, the relative population of the two different isomers depends extremely on experimental conditions.



## MO 21 Molecular Electronics and Energy Transfer

Zeit: Dienstag 10:40–12:40

Raum: H12

**Hauptvortrag**

MO 21.1 Di 10:40 H12

**Molecules in Electronic Circuits: from integrated single molecules to SAMs in CMOS technology** — ●MARCEL MAYOR — University of Basel, Department of Chemistry and Forschungszentrum Karlsruhe GmbH, Institute for Nanotechnology

The integration of molecular structures in electronic circuits is a concept that has already been proposed in the sixties, when Hans Kuhn presented his vision of molecular engineering. Limited by the available techniques, Kuhn and coworkers mainly investigated molecular monolayers deposited on electrodes. In the last few years, the tools to investigate nanoscale objects have improved tremendously, mainly driven by the invention of the scanning probe methods. Furthermore, feature sizes in semiconductor technology have been reduced very fast and continuously. However, this feature size reduction seems to hit soon both, physical and economical limits. With that background, the revival of the idea to integrate molecules in electronic circuits is not surprising.

Molecules are well defined nanoscale objects consisting of a definite structure leading to particular electronic properties. As these structures can be tailored by chemical synthesis, the visionary concept of molecular electronics is geared by the hope that electronic functions can be realized by carefully designed molecular structures.[1] Apart from the huge variety given by the immenseness of possible molecular structures, the incredible smallness of a functional unit based on a molecule is a main driving force. However, integration of molecular structures in electronic circuits is still an experimental challenge and the field is still at the level of exploring the potential as well as the limitations.

In close cooperation with physicists and engineers from academics and industry, single molecules and assemblies of molecules have been integrated in electronic circuits. Correlations between the molecular structure and the observed I/V characteristics have been investigated. The findings allow to further optimize the molecules for particular electronic functions. Several molecular systems have been synthesized and studied to collect the required comprehension to design particular electronic functions. Recently, a molecular rod acting as a single molecule rectifier has been designed, synthesized and integrated.[2] Indeed rectification was observed, however, it does not yet match the rectification ratios known from its silicon opponents.

[1] a) R. L. Carroll, C. B. Gormann, *Angew. Chem. Int. Ed.* (2002) 41, 4378. b) M. Mayor, H. H. Weber, *Chimia* (2002), 56, 494. c) M. Mayor, H. B. Weber, R. Waser in *Nanoelectronics and Information Technology. Advanced Electronic Materials and Novel Devices* (Ed.: R. Waser), Wiley-VCH, Weinheim (2003) 501. d) M. A. Reed, J. M. Tour, *Scientific American* (2000) 282, 86. e) C. Joachim, J. K. Gimzewski, A. Aviram, *Nature* (2000) 408, 541.

[2] M. Elbing, R. Ochs, M. Koentopp, M. Fischer, C. von Hänisch, F. Weigend, F. Evers, H. B. Weber, M. Mayor, *Proc. Natl. Acad. Sci. U.S.A.* (2005) 102, 8815.

**Hauptvortrag**

MO 21.2 Di 11:10 H12

**Single-molecule electronics: Conductance mechanisms** — ●GIANAURELIO CUNIBERTI — Institute for Theoretical Physics, University of Regensburg, D-93040 Regensburg, Germany

Since few years, several quantum transport experiments employing unimolecular systems have been proven. Some of related emerging phenomena, however, are still missing sound theoretical explanations. One principal limitation is the “static” description of molecular bridges typically assumed for transport processes. Molecules, indeed, are flexible objects and their nuclear “dynamics” plays in general a fundamental role in charge transfer as well as transport mechanisms. In this talk, I will give an overview on the role of vibrations and inelastic transport in molecular systems, and show how such phenomena do dramatically affect the overall conduction properties of molecular junctions.

MO 21.3 Di 11:40 H12

**Schwingungsenergie- und Informationstransfer über molekulare Brücken** — ●ULRIKE TROPFMANN, CAROLINE GOLLUB und REGINA DE VIVIE-RIEDLE — Ludwig-Maximilians-Universität, Department Chemie, Butenandtstr. 11, 81377 München

Das Verständnis von intramolekularen Energietransportprozessen ist von grundlegendem Interesse für Fragestellungen, wie Schwingungsumverteilung und damit gekoppelte Reaktionen in komplexen

(bio)molekularen Systemen, oder Elektronen-Transport in molekularen Drähten. Wir untersuchen IVR-Prozesse in eindimensionalen molekularen Brücken am Beispiel linearer  $(C\equiv C)_n$ -Brücken mit den CC-Streckschwingungen als Transport-Moden. Unser Modell-System ist das Octatetraim-Molekül. Ausgehend von numerischen Quantendynamik-Simulationen auf ab initio berechneten Potentialflächen wird ein modularer Ansatz zur Beschreibung der IVR-Prozesse im Bild der Lokalmode vorgestellt. Die Güte dieser Beschreibung wird anhand des Vergleichs mit volldimensionalen Rechnungen abgeschätzt und eine Anwendbarkeit auf höherdimensionale Systeme (längere Ketten) diskutiert. Ziel dieser Arbeiten ist es, den Informationstransfer über Schwingungsumverteilung in molekularen Brücken zu beschreiben und über Laseranregung zu kontrollieren.

MO 21.4 Di 11:55 H12

**Molekulare Schalter als Brücken in Elektronentransfer-Systemen** — ●DOROTHEE GEPPERT und REGINA DE VIVIE-RIEDLE — LMU München, Department Chemie, Butenandtstr. 11, 81377 München

Wir untersuchen Donor-Brücke-Akzeptor-Systeme, durch die ein Energie- oder Elektronentransfer möglich ist. Ein Fulgid als verbrückende Einheit kann, initiiert durch Photochemie, zwischen zwei stabilen Zuständen wechseln, von denen nur ein Isomer einen Elektronentransfer zulässt. Mit quantenchemischen und -dynamischen Methoden wird dieser Schaltprozess genauer untersucht.

Für einen effektiven Schaltprozess muss die über elektronisch angeregte Zustände verlaufende Isomerisierung schnell und vollständig ablaufen. Wir schlagen dafür den Einsatz von geformten Laserpulsen vor, die wir mittels Optimal Control Theory erhalten. Dabei kommen verschiedene Kontrollstrategien zum Einsatz, die an der Isomerisierungsreaktion der funktionalen Untergruppe der Fulgide illustriert werden [1]. Die verschiedenen benutzten Zielzustandsdefinitionen führen zu unterschiedlichen Reaktionspfaden. Während ein intermediäres Target das Wellenpaket durch die konischen Durchschnitte führt, ergibt sich mit einer Zieldefinition im Grundzustand ein Pump-Dump-Reaktionsweg. In diesem Fall lassen sich die optimierten Laserpulse drastisch vereinfachen.

[1] D. Geppert, L. Seyfarth, and R. de Vivie-Riedle, *APB* 79 (2004) 987-992.

MO 21.5 Di 12:10 H12

**Towards Dispersion Free Exciton Diffusion: Ultrafast Förster Transfer in Doped Polymer Films** — ●STEFAN LOCHBRUNNER und MARTIN SCHLOSSER — LS für BioMolekulare Optik, Ludwig-Maximilians-Universität München

In optoelectronic applications of organic thin film systems the absorbed energy is transported by exciton diffusion to the active interface where charge separation occurs. In unordered materials like in most polymers the sites exhibit electronic states with a large energy dispersion and the excitons are trapped at low energy sites. Therefore we propose as active sites chromophores which are incorporated in the polymer matrix but interact only weakly with the polymeric environment. Their electronic states have similar energies and no trapping of the excitons should occur allowing for a dispersion and loss free long range energy transport by Förster transfer between them. To test the approach we performed femtosecond absorption experiments on PMMA films highly doped with perylene bisimide dyes and characterized the energy transfer between the chromophores. We find a stretched exponential time dependence characteristic for Förster energy transfer between immobilized chromophores with a transfer time of 1.5 ps for an average distance of 2.3 nm resulting in a high mobility of the optically generated excitons. We can also collect the energy with high efficiency on dye molecules which exhibit an absorption spectrum that is red shifted compared to the perylene dyes responsible for the exciton diffusion. This opens a design route for artificial light harvesting complexes.

MO 21.6 Di 12:25 H12

**Ultrafast Electronic Dynamics in Ordered Pentacene Films** — ●TOBIAS BITTKAU<sup>1</sup>, STEFAN LOCHBRUNNER<sup>1</sup>, IDA KOZMA<sup>1</sup>, MARTIN HUTH<sup>2</sup>, STEFAN SCHIEFER<sup>2</sup>, and BERT NICKEL<sup>2</sup> — <sup>1</sup>Lehrstuhl für BioMolekulare Optik, LMU München — <sup>2</sup>Department für Physik und CeNS, LMU München

Micro crystalline thin films of organic molecules are frequently used in organic electronics applications, especially for field effect transistors. In case of low defect densities such films can exhibit band transport. Pentacene films for example have a highly ordered, characteristic herring bone structure which seems to be responsible for the extraordinary high exciton mobility in these films. Since charge and energy transport properties are directly linked to the electronic structure and dynamics of the systems, we started investigating electronic excitations in ordered pentacene films with ultrafast absorption spectroscopy. Contrary to time

resolved luminescence experiments, this technique allows also for the observation of non radiating species like polarons. We observe that the excitation induced bleach has a complex recovery kinetics consisting of a 400 fs, a 5 ps, and a some hundred ps component. The localization of the excitation and its dissociation into charged species is discussed with respect to spectral signatures appearing around 630 nm. In addition, we find an unexpected long lasting memory of the excitation polarization which points to highly anisotropic excitation exchange processes.

## MO 22 Spectroscopy in He-Droplets

Zeit: Dienstag 11:40–12:40

Raum: H10

MO 22.1 Di 11:40 H10

**Spektroskopie von Alkali- und Erdalkaliatomen auf  $^3\text{He}$  und  $^4\text{He}$  Nanotröpfchen** — ●OLIVER BÜNERMANN und FRANK STIENKEMEIER — Physikalisches Institut, Universität Freiburg, Hermann Herder Str. 3, D-79104 Freiburg

Aus den beiden Isotopen  $^3\text{He}$  und  $^4\text{He}$  gebildete Nanotröpfchen haben aufgrund ihrer Quantenstatistik stark unterschiedliche Eigenschaften.  $^4\text{He}$ -Nanotröpfchen stabilisieren sich auf eine Temperatur von 380 mK und sind superflüssig. Demgegenüber sind die  $^3\text{He}$ -Nanotröpfchen normalflüssig, obwohl sie eine Temperatur von 150 mK besitzen. Durch einen Vergleich der beiden Systeme ist es möglich, den Einfluss der unterschiedlichen Quanteneigenschaften auf die Wechselwirkung mit Atomen und Molekülen zu untersuchen.

Wir haben Nanotröpfchen mit den Alkaliatomen Lithium und Natrium, sowie mit dem Erdalkalium Strontium dotiert und mit Hilfe von Laser-induzierter Fluoreszenz und Laser-induzierter Strahlabschwächung untersucht. Es zeigt sich, dass die Einlagerungsorte und die Wechselwirkungsenergien für alle drei Atome bei beiden Isotopen vergleichbar sind. Die Absorptionen von Natrium[1] und Strontium sind sehr ähnlich. Die Lithium Spektren unterscheiden sich hingegen sehr.

[1] F. Stienkemeier and O. Bünermann and R. Mayol and F. Ancilotto and M. Barranco and M. Pi, Surface Location of Alkali Atoms in  $^3\text{He}$  Nanodroplets, Phys. Rev. B 70, 214509 (2004)

MO 22.2 Di 11:55 H10

**Spektroskopie an Mg-Atomen in Heliumtropfen** — ●S. GÖDE, A. PRZYSTAWIK, J. TIGGESBÄUMKER und K.-H. MEIWES-BROER — Universität Rostock, Fachbereich 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.

Laserinduzierte Fluoreszenzspektroskopie sowie resonante Zwei-Photonen-Spektroskopie an Magnesiumatomen zeigen, dass sich die Atome im Inneren des Tropfens befinden [1]. Neben einer Verschiebung zu höheren Anregungsenergien beobachtet man eine Aufspaltung des Überganges in zwei Anteile. Diese wurde bisher im Rahmen eines modifizierten Blasenmodells als Quadrupolschwingung des umgebenden Heliums infolge der nichtsphärischen Elektronenverteilung des angeregten Mg-Atoms gedeutet.

Unsere Messungen zeigen nun, dass durch Variation der Tropfen-größe und des Dampfdruck in der Pickup-Zelle die relativen Intensitäten der Aufspaltung verschoben werden. Dabei kann einer der Anteile möglicherweise durch den Einfluss von Van-der-Waals-Komplexen erklärt werden.

[1] J. Reho, U. Merker, M.R. Radcliff, K.K. Lehmann und G. Scoles, J. Chem. Phys. **112**, 8409 (2000)

## MO 23 Photochemistry

Zeit: Dienstag 14:00–16:00

Raum: H12

MO 23.1 Di 14:00 H12

**Ultrafast dissociation and recombination of substituted diarylmethylchlorides** — ●CORD ELSNER<sup>1</sup>, ULI SCHMIDHAMMER<sup>1</sup>, EBERHARD RIEDLE<sup>1</sup>, and HERBERT MAYR<sup>2</sup> — <sup>1</sup>LS für BioMolekulare Optik, Ludwig-Maximilians-Universität München — <sup>2</sup>Department Chemie und Biochemie, Ludwig-Maximilians-Universität München

Derivatives of diarylmethane  $\text{Ar}_2\text{CH-X}$  are well proven precursors for the investigation of the reactivity of diarylcarbenium ions produced by

**Photoelektronenspektroskopie an dotierten Heliumtropfen** — ●ANDREAS PRZYSTAWIK, P. RADCLIFFE, TH. DIEDERICH, J. TIGGESBÄUMKER und K.-H. MEIWES-BROER — Universität Rostock, Institut für Physik, Universitätsplatz 3, 18051 Rostock

In ultrakalten Heliumtröpfchen können mit der Pickup-Technik Atome und Moleküle eingelagert und Cluster gebildet werden. Mittels resonanter Zwei-Photonen-Ionisation ist es möglich, die optischen Spektren kleiner Silber-Cluster zu vermessen [1]. Diese zeigen einen deutlichen Einfluß der Matrix auf die angeregten Cluster.

Die Nutzung der resonanten Ionisation zur Massenselektion erlaubt die Photoelektronenspektroskopie der neutralen Spezies. Diese Methode eignet sich insbesondere zur Untersuchung der angeregten Zustände des Clusters [2]. Weiterhin werden Wechselwirkungen des Photoelektrons mit der Heliummatrix beobachtet. Das Ionisationspotential von Silberclustern im Heliumtropfen ändert sich nur geringfügig im Vergleich zur Gasphase.

[1] F. Federmann, K. Hoffmann, N. Quaas und J.P. Toennies, Eur. Phys. J. D **9**:11 (1999)

[2] P. Radcliffe, A. Przystawik, Th. Diederich, T. Döppner, J. Tiggesbäumker und K.-H. Meiwes-Broer, Phys. Rev. Lett. **92**:173403 (2004)

MO 22.4 Di 12:25 H10

**IR-Phononenseitenbänder von Methan in Heliumnanotröpfchen** — ●STEPHAN RUDOLPH, GÖTZ WOLLNY, KLAUS VON HAEFTEN und MARTINA HAVENITH — Lehrstuhl für Physikalische Chemie 2, Ruhruniversität Bochum

Heliumnanotröpfchen sind Prototypen für eine "finite-size" - Quantenflüssigkeit. Wir möchten die kollektiven Anregungen in Heliumnanotröpfchen genauer untersuchen.

Als neue Strahlungsquelle für das mittlere Infrarot wird ein cw-optoparametrischer Oszillator (OPO) vorgestellt, der die Spektroskopie von ultrakalten Gasen im mittleren Infrarot-Bereich des elektromagnetischen Spektrums ermöglicht. Der OPO stellt eine Strahlungsquelle mit hoher Leistung (max. 2,9 W), breiter Durchstimmbarkeit (2,9-3,9  $\mu\text{m}$ ) und schmaler Linienbreite ( $< 1$  MHz) dar.

Es konnten auf Grund dieser hohen Leistung erstmalig Phononenseitenbänder der Anregung von Methan in Heliumnanotröpfchen im Infraroten gemessen werden. Dazu wurde die Leistungsabhängigkeit der gemessenen Spektren näher untersucht.

Durch die Variation des Pick-up-Druckes konnten die Bänder eindeutig dem Monomer und verschiedenen Multimeren zugeordnet werden.

Diese Arbeiten wurden durch das Schwerpunktprogramm 1116 der DFG finanziell unterstützt.

the photoinitiated dissociation to  $\text{Ar}_2\text{CH}$  and X. On the microsecond timescale both the radicals and the ions are detected optically. It has, however, been reported that the relative yield of the two product pairs depends strongly on the substitution and the solvent. We have now investigated the primary dissociation process and the subsequent subnanosecond kinetics with tuneable UV excitation and broadband UV to visible detection with sub-100 fs resolution. At 330 nm we can observe the concentration of the radicals and at 430 nm the diarylcarbenium ions.

We find that the dissociation proceeds in just a few hundred femtoseconds. In about 10 ps part of the radicals convert to ions, presumably by electron transfer between the closely spaced radical pair. Within the next 100 to 200 ps a sizable fraction of the ions recombines to the diarylmethyl compound. This means that only after this time the ions separate sufficiently to avoid geminate recombination and further recombination will occur with diffusion limited speed. The specifics of the processes can be tuned by suitable substitution of the basic diarylmethylchloride. This allows the comparison of the geminate recombination probability with the known "macroscopic" reactivity.

MO 23.2 Di 14:15 H12

**Precursormoleküle durch kurze Laserpulse: Quantenchemische und quantendynamische Studien an Diphenylmethylchlorid** — ●BENJAMIN P. FINGERHUT, DOROTHEE GEPPERT und REGINA DE VIVIE-RIEDLE — LMU München, Department Chemie, Butenandt-Str. 11, 81377 München

Diphenylmethyl-Kationen treten in biologischen und chemischen Prozessen als reaktive Intermediate auf. Über photochemische Anregung können neue Precursor-Moleküle dieser Art gezielt erzeugt werden. Die Bildung dieser Carbokationen durch laserinduzierte Dissoziation wird auf der Femtosekunden-Zeitskala untersucht.

Um die optische Anregung sowie die Dissoziation der C-Cl-Bindung zu beschreiben, müssen mindestens drei elektronische Zustände berücksichtigt werden. Entscheidend für die Reaktion sind ein  $\pi^* - \sigma^*$ -Charge-Transfer, der den optisch zugänglichen  $\pi^*$ -Zustand im Franck-Condon-Bereich mit einem dissoziativen  $\sigma^*$ -Reaktionskanal verbindet, sowie ein weiterer strahlungsloser Relaxationsprozess, der für die Verzweigung zu den konkurrierenden homolytischen und heterolytischen Reaktionskanälen entscheidend ist.

Die photochemisch induzierte Dissoziation der  $\sigma$ -C-Cl-Bindung einschließlich der Molekül-Laserwechselwirkung wird anhand von 1D-ab-initio Potentialkurven quantendynamisch beschrieben und der Bildungszeitraum der Fragmente mit experimentellen Ergebnissen verglichen. Darüberhinaus wird der Einfluss verschiedener polarer Lösungsmittel auf die energetische Reihenfolge der Reaktionskanäle diskutiert.

MO 23.3 Di 14:30 H12

**Aufklärung der Photodissoziationsdynamik von SPC13 bei 235 nm mittels 3D-Imaging** — ●SEBASTIAN KAUCZOK<sup>1,2</sup>, KARL-HEINZ GERICKE<sup>1</sup>, CHRISTOF MAUL<sup>1</sup>, NIELS GOEDECKE<sup>1</sup>, ALEXEY CHICHININ<sup>2</sup> und OLIVER OTT<sup>1</sup> — <sup>1</sup>Institut für Physikalische und Theoretische Chemie, TU-Braunschweig — <sup>2</sup>Institute of Chemical Kinetics and Combustion, Novosibirsk, Russia

Die Photodissoziation von Thiophosphorylchlorid (Punktgruppe C<sub>3v</sub>) wurde mithilfe der 3D-Imaging Methode untersucht, die es erlaubt alle drei Komponenten des Impulsvektors individueller Photofragmente quantenzustandsaufgelöst zu beobachten. Chloratome im Grundzustand und im Spin-Bahn-angeregten Zustand wurden dabei mit einer Kombination aus der REMPI-TOF-Technik mit einem orts- und zeitauflösenden Delay-Line Detektor nachgewiesen. Die Geschwindigkeitsverteilungen und die geschwindigkeitsabhängige räumliche Anisotropie konnten so ermittelt werden. Hieraus können Rückschlüsse auf die bei der Photolyse ablaufenden Elementarprozesse gezogen werden, wobei auch aufgrund der Energiebilanz eine Unterscheidung von Primär- und Sekundärphotolyse prinzipiell möglich ist. Außerdem wurden erste Vorarbeiten für die Photodissoziation von Dichlormethan bei 193 nm im Zwei-Farben-Experiment geleistet.

MO 23.4 Di 14:45 H12

**Are branching ratios in the photodissociation of CCl<sub>4</sub> isotope specific?** — ●CHRISTOF MAUL — Institut für Physikalische und Theoretische Chemie, TU Braunschweig, 38106 Braunschweig, Germany

Photodissociation of CCl<sub>4</sub> in the ultraviolet produces chlorine atoms in their ground [Cl(<sup>2</sup>P<sub>3/2</sub>)] and excited spin-orbit [Cl\*(<sup>2</sup>P<sub>1/2</sub>)] states. In 1994, Deshmukh and Hess, reported isotope specific relative yields  $\phi$  in the photodissociation of CCl<sub>4</sub> where  $\phi$  is defined as the percentage of Cl atoms in a given spin-orbit state. In particular,  $\phi(^{35}\text{Cl}^*)$  was reported to be 0.20 while  $\phi(^{37}\text{Cl}^*)$  was found to be 0.44. The data were obtained from integrated intensities of line profiles monitored for Cl/Cl\* detection by (<sup>2</sup>+1) resonance enhanced multiphoton ionization (REMPI) where <sup>35</sup>Cl and <sup>37</sup>Cl isotopes were separated in a time-of-flight spectrometer. No explanation was given for the alleged phenomenon.

In order to verify the observation of isotope specific branching ratios the CCl<sub>4</sub> photodissociation was reinvestigated. Instead of comparing in-

tegrated line intensities for different electronic transitions of one selected isotope, the isotopic distribution for five carefully chosen electronic transitions was monitored. Thus, the laser intensity could be adjusted to signal intensity, and changes in laser intensity affected both isotopes in the same way. For all transitions the observed isotopic fragment distribution was found to be equal to the natural distribution within experimental error. Thus, it must be concluded that branching ratios in the photodissociation of CCl<sub>4</sub> are not isotope specific.

MO 23.5 Di 15:00 H12

**Time Resolving a Nucleophilic Addition** — ●LAIMGRUBER STEFAN, HILMAR SCHACHENMAYR, WOLFGANG SCHREIER, and PETER GILCH — Department für Physik, Ludwig-Maximilians-Universität, Oettingenstr. 67, D-80538 München, Germany

Nucleophilic additions to double bonds are among the most important elementary reactions in organic chemistry. Detailed mechanistic information on these reactions are difficult to obtain. They usually proceed thermally and are therefore not accessible by femtosecond spectroscopy. During the photoreaction of *o*-nitrobenzaldehyde to *o*-nitrosobenzoic acid a ketene intermediate is formed [1]. The formation of this *ground state* species is ultrafast ( $\sim 400$  fs) and its formation time is hardly affected by the solvent. Thanks to this fast formation a nucleophilic addition to the ketene can easily be time resolved. We monitored the kinetics of this addition by means of visible and vibrational femtosecond spectroscopy and observed reaction times ranging from 10 ps to some nanoseconds depending on the solvent used. Based on these findings conclusions on the mechanism of the addition will be presented.

[1] S. Laimgruber et al., Angew. Chem. Int. Ed. 44 (2005) 7901

MO 23.6 Di 15:15 H12

**Charakterisierung neuartiger Photoschalter zur Beobachtung ultraschneller Faltungsprozesse in Modellpeptiden** — ●THORBEN CORDES<sup>1</sup>, TORSTEN SCHADENDORF<sup>2</sup>, STEPHAN HERRE<sup>2</sup>, KAROLA RÜCK-BRAUN<sup>2</sup> und WOLFGANG ZINTH<sup>1</sup> — <sup>1</sup>Lehrstuhl für BioMolekulare Optik, Oettingenstr. 67, Ludwig-Maximilians-Universität München, 80538 München — <sup>2</sup>Technische Universität Berlin, Institut für Chemie, Straße des 17. Juni 135, 10623 Berlin

In der Vergangenheit wurden ultraschnelle Prozesse in der Protein- und Peptidfaltung durch auf Azobenzol basierende Schalter (APB/AMPB) ermöglicht. Durch schnelle E/Z-Isomerisierung können Strukturänderungen im anhängenden Peptidteil getriggert werden und durch transiente Absorptionsspektroskopie im sichtbaren oder infraroten Spektralbereich beobachtet werden. Es werden neue Moleküle gesucht, die ähnliche Triggereigenschaften aufweisen und sich leicht in Peptide integrieren lassen. Die von uns untersuchten neuartigen Hemithioindigoverbindungen (HTI-Photoschalter) besitzen viertersprechende Eigenschaften. Sie sind durch Licht im sichtbaren Spektralbereich reversibel von E nach Z schaltbar und beide Isomere weisen eine große thermische Stabilität auf. Der Isomerisierungsprozess läuft hierbei im Bereich einiger 10 ps ab. Die photochemischen Eigenschaften (Absorption, Schaltquantenausbeuten, Fluoreszenzeigenschaften) der HTI-Photoschalter und der Ablauf ihrer Isomerisierung werden vorgestellt. Insbesondere werden die Einflüsse von Substituenten und ihrer Position auf die Isomerisierung näher untersucht.

MO 23.7 Di 15:30 H12

**Ultraschnelle Dynamik der Ringöffnungs-Reaktion eines Indolyl-Fulgimids** — ●SIMONE DRAXLER<sup>1</sup>, STEPHAN MALKMUS<sup>1</sup>, FLORIAN KOLLER<sup>1</sup>, THOMAS BRUST<sup>1</sup>, CHRISTINE SCHULZ<sup>2</sup>, STEFFEN DIETRICH<sup>2</sup>, KAROLA RÜCK-BRAUN<sup>2</sup>, WOLFGANG ZINTH<sup>1</sup> und MARKUS BRAUN<sup>1</sup> — <sup>1</sup>Ludwig-Maximilians-Universität München, Lehrstuhl für BioMolekulare Optik, Oettingenstr. 67, 80538 München — <sup>2</sup>Technische Universität Berlin, Institut für Chemie, Straße des 17. Juni 124, 10623 Berlin

Fulgimide sind molekulare Schalter, die über Lichtanregung reversibel eine strukturelle Änderung erfahren. Dabei werden auch die optischen Eigenschaften beeinflusst, so dass sich ein ausgeprägtes photochromes Verhalten zeigt. Bei N-Methyl-Indolyl-Fulgimid existieren drei Isomere (C, E und Z), die thermisch stabil sind, wobei das C-Isomer im sichtbaren Spektralbereich eine ausgeprägte Absorption aufweist, die keinen spektralen Überlapp mit der Absorption des E- oder Z-Isomers hat. Es wurde die lichtinduzierte Ringöffnungs-Reaktion C nach E eines photochromen Indolyl-Fulgimids mittels Femtosekunden-Pump-Probe-Spektroskopie im sichtbaren und mittleren infraroten Spektralbereich untersucht [1]. Hierbei wurde eine exponentielle 2,1 ps Dynamik des an-

geregten Zustands beobachtet, die der Ringöffnungsreaktion zugeordnet werden kann. Des Weiteren findet man eine nicht-exponentielle 20 ps Komponente, die mit dem Kühlen der heißen Moleküle im elektronischen Grundzustand erklärt wird.

[1] S. Malkmus et al., Chem. Phys. Lett. 417 (2005) 266

MO 23.8 Di 15:45 H12

**System and environment influences on controlled ultrafast dynamics** — •JUDITH VOLL, DOROTHEE GEPPERT, and REGINA DE VIVIE-RIEDLE — LMU Department Chemie, Butenandtstr.11, 81377

In our group a model system for molecular switches was developed. The degrees of freedom of the active center were reduced to relevant reactive coordinates on the essential timescale. Highly accurate quantum chemical calculations lead to two dimensional electronic potential energy surfaces

with conical intersections enabling a coupling between them. On these potential surfaces exact ultrafast quantum dynamics on the femtosecond timescale is performed following laser excitation. Optimal Control Theory made it possible to control the reaction by applying optimized differently shaped laser pulses [1]. Diverse modifications of the reduced model lead to a more realistic behaviour of the system. We augmented the single conical intersections to a seam of conical intersections and examined different barriers on the excited state. These could be induced by mixing with higher electronic states, additional steric groups or solvent effects. In first attempts to understand the influence of the solvents motion on our systems dynamics we use potential surfaces oscillating in time. \Zitat{1}{D. Geppert, L. Seyfarth and R. de Vivie-Riedle, App. Phys. B, 79 (2004) 987-992}

## MO 24 High Resolution Spectroscopy

Zeit: Dienstag 14:00–16:00

Raum: H10

MO 24.1 Di 14:00 H10

**Determination of the excited state structure of 7-azaindole using a Franck-Condon analysis** — •ROBERT BRAUSE, MICHAEL SCHMITT, and KARL KLEINERMANN — Institut für physikalische Chemie I, Heinrich-Heine-Universität, Universitätsstrasse 26.43, 40225 Düsseldorf

The change of the 7-azaindole structure upon electronic excitation was determined by a Franck-Condon analysis of the intensities in the fluorescence emission spectra obtained via excitation of six different vibronic bands. A total of 107 emission band intensities were fit, together with the changes of rotational constants of four 7-azaindole isotopomers. The geometry change of the ring framework upon electronic excitation from the electronic ground state to the  $^1L_b$  state ( $\pi\pi^*$ ) can be described by an overall expansion of the pyridine ring of 7-azaindole, with minor changes of the pyrrole ring. The resulting geometry changes are interpreted on the basis of *ab initio* calculations.

MO 24.2 Di 14:15 H10

**The influence of nuclear spin statistics on femtosecond degenerate four wave mixing spectroscopy of polyatomic systems** — •MAKSIM I. KUNITSKI, CHRISTOPH RIEHN, VICTOR V. MATYLITSKY, and BERNHARD BRUTSCHY — Institute of Physical and Theoretical Chemistry, Johann Wolfgang Goethe-University Frankfurt/M., Marie-Curie-Str. 11, D-60439 Frankfurt/M., Germany

Recently, femtosecond time-resolved degenerate four-wave mixing (fs DFWM) has been introduced as a new technique for high-resolution molecular spectroscopy. We have applied this kind of spectroscopy for investigating nitromethane ( $CH_3NO_2$ ) at room temperature. In the fs DFWM spectrum of  $CH_3NO_2$  new recurrences of *A*-type with a period of  $1/(8A)$  and an additional intensity modulation were discovered [1]. Also, new recurrences of *J*-type with a period of  $1/[4(B+C)]$  were assigned by us in the fs DFWM spectra of  $SO_2$  and  $NO_2$ , *A*, *B* and *C* being the rotational constants. The incorporation of nuclear spin statistics (NSS) into our fs DFWM simulation model allows us to successfully reproduce all these new features. It will be discussed in detail that the symmetry exclusion of certain rotational levels by NSS can cause a regular pattern in the frequency domain. Consequently, this can lead to new time-domain recurrences. Thus the amount of information obtainable from fs DFWM spectra is increased and the understanding of such spectra significantly improved.

[1] C. Riehn, M. I. Kunitski, V. V. Matylitsky, M. F. Gelin, and B. Brutschy, *Phys. Chem. Chem. Phys.* **7**, 3955 (2005).

MO 24.3 Di 14:30 H10

**Laborspektroskopische Untersuchungen an reinen Kohlenstoff-Kettenmolekülen** — •THOMAS GIESEN, PETRA NEUBAUER-GUENTHER und MICHAEL CARIS — I. Physikalisches Institut, Universität zu Köln, Zùlpicher Strasse 77, 50937 Köln

Reine Kohlenstoff-Kettenmoleküle der Form  $C_n$  ( $n=2, 3, 4, \dots$ ) sind die molekularen Bausteine, aus denen sich ringförmige und dreidimensionale Kohlenstoff-Cluster bilden. Zu den bekanntesten Strukturen zählen die Fullerene und Kohlenstoff-Nanoröhrchen. Der Bildungsmechanismus reiner Kohlenstoff-Moleküle aus atomarem Kohlenstoff ist kaum verstanden. Mit Hilfe der hochauflösenden Infrarot-Diodenlaser-Spektroskopie lassen sich jedoch die Struktur und die interne Schwingungsdynamik kleiner

Kohlenstoff-Cluster genauestens untersuchen und aus den gewonnenen Absorptionsspektren ihre Struktur ableiten. Zu diesem Zweck verwenden wir Überschall-Düsenstrahlapparaturen, mit denen sich eine Vielzahl kleiner und mittelgroßer Cluster erzeugen lassen. Die Moleküle  $C_n$  ( $n=3,4,\dots,10, 13$ ) wurden auf diese Weise erzeugt und untersucht. Der Vortrag gibt einen kurzen Überblick über den apparativen Aufbau und die bereits erzielten Ergebnisse.

MO 24.4 Di 14:45 H10

**Infrarot-Laser-Absorptionsspektroskopie heißer Banden von linearem  $C_7$**  — •PETRA NEUBAUER-GUENTHER und THOMAS F. GIESEN — I. Physikalisches Institut, Universität zu Köln, Zùlpicher Str. 77, 50937 Köln

Reine Kohlenstoffmoleküle spielen eine wichtige Rolle in der Chemie des interstellaren Mediums. Sie sind jedoch nicht nur von astrophysikalischer Relevanz, auch die Struktur unterschiedlich großer Kohlenstoffcluster ist Gegenstand aktueller Forschung. Kleine Cluster aus einigen wenigen Atomen liegen als Kettenmoleküle vor. Fragen, wie etwa die nach der Starrheit dieser Ketten bezüglich ihrer Biegeschwingung, lassen sich mit Hilfe hochauflösender Spektroskopie genauestens untersuchen. Coupled-Cluster Rechnungen von P. Botschwina (2002) [1] zeigen beispielsweise, dass das Knickschwingungspotential von linearem  $C_7$  keineswegs so flach ist, wie es gemäß der Auslegung bisheriger experimenteller Daten [2] sein müßte. Um Informationen über die Knickschwingungen zu erhalten, untersucht man heiße Banden, die durch den Übergang aus einer Knickschwingung in eine Kombination von Knick- und antisymmetrischer Streckschwingung entstehen. Diese heißen Banden liegen wie die antisymmetrischen Streckschwingungen im mittleren Infrarotbereich. In unserem Labor werden die Kohlenstoffketten in einer Ablationsquelle erzeugt und mittels eines hochauflösenden Diodenlaserspektrometers untersucht. Wir stellen Messungen der  $\nu_4 + \nu_{11} \leftarrow \nu_{11}$  heißen Bande im Bereich von  $2137 \text{ cm}^{-1}$  sowie deren Interpretation vor.

[1] P. Botschwina, Chem. Phys. Lett. 354, 148, 2002

[2] J.R. Heath, R.J. Saykally, J. Chem. Phys. 94, 1724, 1991

MO 24.5 Di 15:00 H10

**Höchstauflösende Terahertz Spektrometer für die Molekülspektroskopie** — •FRANK LEWEN — I. Physikalisches Institut, Universität zu Köln, Zùlpicher Str. 77, 50937 Köln

In diesem Beitrag werden die Kölner Terahertzspektrometer vorgestellt, die für die Laborastrophysik entwickelt wurden und im Frequenzbereich von 53 GHz bis ca. 2.7 THz eingesetzt werden. Generell sind in diesem Frequenzbereich des elektromagnetischen Spektrums abstimmbare und leistungsstarke Strahlungsquelle rar und nicht kommerziell verfügbar. Um diesen Frequenzbereich komplett abdecken zu können, verfolgen wir in Köln 3 Methoden: a) Einsatz von phasengelockten Rückwärtswellenoszillatoren (BWOs) als Fundamentaloszillatoren im Bereich bis 1250 GHz b) Kombination von BWOs und nachgeschalteten Frequenzvervielfacher mit neuartigen Übergitterstruktur-Bauteilen c) Erzeugung von Seitenbänder, die bei der Frequenzmischung eines Terahertzferinfrarotlasers mit einem BWO entstehen und in Köln erfolgreich bis 2 THz eingesetzt werden. Die Meßgenauigkeit liegt bei den hier beschriebenen Methoden zwischen 0.5 und 100 kHz und ist von der Physik des beobachteten Übergangs abhängig. Die Strahlungsquellen sind alle mittels einer Phasenregelung stabilisiert und in der Frequenz an ein Rubidi-

um Frequenznormal angebunden. Die extrem hohe Meßgenauigkeit und der breite Abstimmbereich der Kölner Spektrometer erlauben z. B. eine präzise Messung von Rotationspektren astrophysikalisch relevanter Moleküle, Radikale, Ionen und Atomen. Die gewonnenen Daten werden der Kölner Datenbank für Molekülspektroskopie ([www.cdms.de](http://www.cdms.de)) als Referenz zur Verfügung gestellt.

MO 24.6 Di 15:15 H10

**Hochaufgelösende Rotationspektroskopie an deuteriertem Ammoniak oberhalb von 1.5 THz** — ●CHRISTIAN ENDRES<sup>1</sup>, FRANK LEWEN<sup>1</sup>, HOLGER S.P. MÜLLER<sup>1</sup>, THOMAS GIESEN<sup>1</sup> und DIMITRY G. PAVELIEV<sup>2</sup> — <sup>1</sup>I. Physikalisches Institut, Universität zu Köln — <sup>2</sup>Department of Radiophysics, N.Novgorod State University, Russia

Aufgrund der technologischen Schwierigkeiten bei der Herstellung kompakter, frequenzgenauer, breitbandig abstimmbarer Strahlungsquellen bei THz Frequenzen, ist dieser Spektralbereich spektroskopisch bisher wenig erforscht. Ein von uns erfolgreich verfolgter Ansatz ist die Frequenzvervielfachung der monochromatischen Strahlung, die in unseren Spektrometern von phasenstabilisierten Backward Wave Oscillatoren erzeugt wird. Die Harmonischen höherer Ordnung werden von einem neuartigen Übergitter generiert und konnten bis zur 11. Ordnung erfolgreich zur Aufnahme von hochaufgelösten Rotationspektren bis zu 2.7 THz eingesetzt werden. Auf diese Weise haben wir zahlreiche Spektren von deuteriertem Ammoniak im Frequenzbereich zwischen 0.1 und 2.6 THz mit Mikrowellengenauigkeit aufgenommen und konnten dadurch die Genauigkeit der Rotationsübergänge und der spektroskopischen Konstanten substantiell verbessern. Neben der Präsentation dieser Spektren und deren spektroskopischer Analyse, erfolgt eine technische Beschreibung der eingesetzten Spektrometer.

MO 24.7 Di 15:30 H10

**Submillimeter Spektroskopie an C<sub>3</sub>H - Ein Beispiel für Coriolis-Wechselwirkung und starke Renner-Teller-Kopplung** — ●MICHAEL CARIS, HOLGER S.P. MÜLLER, FRANK LEWEN und THOMAS F. GIESEN — I. Physikalisches Institut Universität zu Köln, Zülpicherstr. 77, 50937 Köln

Das neu entwickelte Kölner „Supersonic Jet Spectrometer for Terahertz Applications“ (SuJeSTA) wurde zur Untersuchung des linearen X<sup>2</sup>Π Propynylidyne Radikales (I-C<sub>3</sub>H) eingesetzt. Mit SuJeSTA

wurden erstmals Übergänge der  $\nu_4$  ( ${}^2\Sigma^u$ ) CCH-Knickschwingung gemessen, die aufgrund des starken Renner-Teller-Effekts im Submillimeter-Wellenlängenbereich liegt. Acht gemessene Linien konnten Vibrationsübergängen zwischen dem Grundzustand ( ${}^2\Pi$ ) und dem ersten angeregten Zustand  $\nu_4 = 1$  ( ${}^2\Sigma^u$ ) zugeordnet werden. Weiterhin wurde das reine Rotationsspektrum von C<sub>3</sub>H bis 600 GHz untersucht und der Bereich der gemessenen Übergänge aus früheren Arbeiten erweitert (Yamamoto *et al.* von 1990 [1]). Insgesamt konnten 43 reine Rotationsübergänge in den Vibrationsgrundzuständen ( ${}^2\Pi_{1/2}$ ,  ${}^2\Pi_{3/2}$ ) und im ersten angeregten Zustand  $\nu_4 = 1$  ( ${}^2\Sigma^u$ ) gemessen werden. Der neu angepasste Parametersatz ermöglicht verlässliche Frequenzvorhersagen bis zu 1 THz. Die ermittelte Energie des  $\nu_4$  ( ${}^2\Sigma^u$ ) Zustandes liegt 609977,1(42) MHz über dem Grundzustand. Der Aufbau des neuen Spektrometers und die Ergebnisse der C<sub>3</sub>H-Messungen werden vorgestellt.

[1] S. Yamamoto, S. Saito, H. Suzuki, S. Deguchi, N. Kaifu, S. Ishikawa, and M. Ohishi, *Ap. J.*, **348**, 363–369 (1990).

MO 24.8 Di 15:45 H10

**The C<sub>2v</sub> Structure of Acetylacetone** — ●JENS-UWE GRABOW<sup>1</sup> and WALTHER CAMINATI<sup>2</sup> — <sup>1</sup>Universität Hannover, Institut für Physikalische Chemie und Elektrochemie, Callinstr. 3-3A, D-30167 Hannover — <sup>2</sup>Dipartimento di Chimica “G. Ciamician” dell’Università, Via Selmi 2, I-40126 Bologna, Italien

Acetylacetone allows for several tautomeric forms at different conformations in dynamic equilibrium and multiple pathways of internal motions between equivalent configurations; together with malonaldehyde it can be considered a prototype molecule for studying keto-enol tautomerization. We present here the pure rotational spectrum of enolic acetylacetone, measured in supersonic expansions, which provides strong evidence for the symmetric nature of the internally highly dynamic molecule.

It has often been postulated that the lowest energy enolic form of Acetylacetone assumes C<sub>s</sub> symmetry, i.e., has a double-minimum potential possibly exhibiting a low barrier to internal proton transfer and not a single minimum, C<sub>2v</sub>. Recent theoretical calculations and experimental work support the C<sub>s</sub> hypothesis but the literature on this fascinating molecule is divided. Towards this objective, the high-resolution rotational spectra of enolic acetylacetone and 3 isotopologues have been obtained, revealing C<sub>2v</sub> symmetry. The two methyl groups exhibit a very low barrier to internal rotation, thus making acetylacetone internally highly dynamic.

## MO 25 Poster: Electronic Spectroscopy

Zeit: Dienstag 16:30–18:30

Raum: Labssaal

MO 25.1 Di 16:30 Labssaal

**Laser induced emission of the fully correlated electron pair from a quantum dot.** — ●OLEG KIDUN and DIETER BAUER — Max-Planck-Institut fuer Kernphysik, Heidelberg,

The exactly solvable problems of two electrons coupled by the Coulomb interaction can be used as unique tests for any approximate theory that deals with few-body systems and related experiments [1,2]. We use the two-electron states of the parabolic potential well and the two-electron states in a strong electromagnetic field to calculate the time evolution of the emission probability of electron pairs. As an example, we compare the sequential double ionization, which is the conventional one-particle description of multielectron ejection, and the solution based on two-electron correlated states [3]. The entanglement and the conditions of separability of these correlated states are discussed.

[1] M. Taut, A. Ernst, H. Eschrig, *J. Phys. B* **31**, 2689 (1998)

[2] D. Bauer, *Phys. Rev. A* **56**, 3028 (1997)

[3] O. Kidun, N. Fominykh, J. Berakdar, *J. Phys. B* **36**, 1 (2003)

MO 25.2 Di 16:30 Labssaal

**Lifetime vibrational interference effects studied in the NO<sup>+</sup>(A<sup>1</sup>Π → X<sup>1</sup>Σ<sup>+</sup>) fluorescence after 1s<sup>-1</sup>π\* resonance excitation** — ●S KLUMPP<sup>1</sup>, L WERNER<sup>1</sup>, A EHRESMANN<sup>1</sup>, PH V DEMEKHIN<sup>2</sup>, M P LEMESHKO<sup>2</sup>, V L SUKHORUKOV<sup>2,3</sup>, K-H SCHARNTER<sup>4</sup>, and H SCHMORANZER<sup>3</sup> — <sup>1</sup>Institut für Physik, Universität Kassel — <sup>2</sup>Rostov State University of Transport Communications, Rostov-on-Don — <sup>3</sup>Fachbereich Physik, TU Kaiserslautern — <sup>4</sup>I. Physikalisches Institut, Universität Giessen

NO<sup>+</sup>(A<sup>1</sup>Π → X<sup>1</sup>Σ<sup>+</sup>) fluorescence after the de-excitation of the 1s<sup>-1</sup>π\* resonance of N\*O and NO\* has been studied in the fluorescence range

between 118 nm and 142 nm. The measured cross sections for the A<sup>1</sup>Π(v') → X<sup>1</sup>Σ<sup>+</sup>(v'') fluorescence were compared with calculated ones taking into account lifetime vibrational interference (LVI) between pathways connected with different vibrational 1s<sup>-1</sup>π\*(v<sub>r</sub>) levels. Especially in the case for the NO\* core-excited state the complex dependence of the computed cross sections for the A-X fluorescence on the exciting-photon energy and on v' and v'' is connected with LVI.

MO 25.3 Di 16:30 Labssaal

**B state vibrational progression and predissociation of Br<sub>2</sub> in Ar matrix** — ●HEIDE IBRAHIM<sup>1</sup>, MARKUS GÜHR<sup>1,2</sup>, and NIKOLAUS SCHWENTNER<sup>1</sup> — <sup>1</sup>Institut für Experimentalphysik, Freie Universität Berlin, D-14195 Berlin — <sup>2</sup>Stanford Synchrotron Radiation Laboratory, Menlo Park, California 94025-7015

Using a narrow linewidth dye laser in the visible range (530 nm to 640 nm) we record high resolution excitation spectra of Br<sub>2</sub> in solid Ar, covering the whole vibrationally structured region of the electronic B state. We find narrow features (Zero Phonon Lines with isotope splitting) and structured Phonon Side Bands, reflecting the phonon density of states of the Ar crystal. We detect NIR fluorescence of A, A' and B state simultaneously with a broadband detector. A two dimensional plot of highly resolved fluorescence versus scanned excitation wavelength illustrates the B state vibrational progression and population transfer from B to the deeper lying A and A' states. From the systematic behaviour of zero phonon linewidth, vibrational spacing and intensities we identify two cross regions with repulsive states and the corresponding coupling strength.

MO 25.4 Di 16:30 Labsaal

**REMPI-Spektroskopie von Methylamin** — ●MOANA NOLDE und KARL-MICHAEL WEITZEL — Philipps-Universität Marburg, FB Chemie, Hans-Meerwein-Str, 35032 Marburg

Die Spektren der Rydbergzustände für Ammoniak sind in den letzten Jahrzehnten gut durch die REMPI-Spektroskopie untersucht worden. In vorhergehenden Arbeiten [1] haben wir die Spektren des  $\tilde{C}'$ -Rydbergzustands aller Ammoniakisotopomere erhalten und charakterisiert. Durch die Substitution eines Wasserstoffatoms im  $\text{NH}_3$  durch eine Methylgruppe erhält man Methylamin ( $\text{CH}_3\text{NH}_2$ ), dessen Rydbergzustände bisher wesentlich weniger gut beschrieben sind als die des Ammoniaks. Durch die zusätzlichen Schwingungsfreiheitsgrade erwartet man eine wesentlich komplexere Schwingungsstruktur als beim  $\text{NH}_3$ . In diesem Beitrag untersuchen wir die REMPI-Spektren des Methylamins ( $\text{CH}_3\text{NH}_2$ ). Diese zeigen klare Progressionen der  $\nu_9$ -,  $\nu_7$ -Schwingungen und der  $\nu_7 + n \cdot \nu_9$ -Kombinationsschwingung. Zur Aufklärung von Tunnel-Effekten in der Moleküldynamik werden derzeit Experimente mit deuteriertem Methylamin durchgeführt.

[1] M. Nolde, K.-M. Weitzel, C. M. Western, PCCP **7** (2005), 1527-1533.

MO 25.5 Di 16:30 Labsaal

**Excitation Spectroscopy of ClF in an Argon Matrix** — ●NINA OWSCHIMIKOW, MIZUHO FUSHITANI und NIKOLAUS SCHWENTNER — Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin

We investigate the B state dynamics of chlorine monofluoride (ClF) molecules embedded in a solid Argon (Ar) matrix at liquid helium temperature for laser excitation wavelengths below and above the gas phase dissociation limit (476 nm). The ClF molecule occupies a single substitutional site in the Ar lattice, and is therefore capable of librational motion [1] and rapid reorientation [2] upon excitation. Frequency resolved excitation spectra of the B state were obtained by monitoring the intensity of the A' fluorescence. In contrast to results for the non-rotating molecules Cl<sub>2</sub> and Br<sub>2</sub> the excitation spectra of ClF show no resolved vibrational progression even below the gas dissociation limit. This indicates a large contribution of librational modes to the vibronic transition. Therefore we study the depolarization and thus dynamics of reorientation on ultrafast (ps) and slow (ms) timescales. Additionally, we investigate the bleaching efficiency and its dependence on the excitation wavelength.

[1] T. Kiljunen, M. Bargheer, M. Gühr, N. Schwentner, and B. Schmidt, PCCP **6**, 2932 (2004)

[2] M. Bargheer, M. Gühr, and N. Schwentner, J. Chem. Phys. **117**, 5 (2002)

## MO 26 Poster: Photochemistry

Zeit: Dienstag 16:30–18:30

Raum: Labsaal

MO 26.1 Di 16:30 Labsaal

**The role of superexcited states in photoionization and photofragmentation of HCl** — ●CHRISTOF MAUL<sup>1</sup>, KARL-HEINZ GERICKE<sup>1</sup>, and ALEXEY CHICHININ<sup>1,2</sup> — <sup>1</sup>Institut für Physikalische und Theoretische Chemie, TU Braunschweig, 38106 Braunschweig, Germany — <sup>2</sup>Institute of Chemical Kinetics and Combustion, Russian Academy of Sciences, 630090 Novosibirsk, Russia

HCl is known for competition of ionization and fragmentation when excited by two-photon absorption from its ground state  $X^1\Sigma^+$  into the  $B^1\Sigma^+$  state. The competition between fragmentation and ionization is initiated by absorption of a third photon, yielding either  $\text{HCl}^+$  or electronically excited  $\text{H}^*$  and  $\text{Cl}^*$  fragments. These species will produce  $\text{H}^+$  and  $\text{Cl}^+$  by absorption of a fourth photon. Besides the ground ionic state  $X^2\Pi$  a multitude of neutral, mostly Rydberg, states are accessible by absorption of the third photon. These Rydberg states are called superexcited if they lie at higher energies than the molecular ionization potential.

Observing speed and spatial distributions of  $\text{H}^+$ ,  $\text{Cl}^+$ , and  $\text{HCl}^+$ , one can determine the nature of the states accessed after absorption of the third photon. The  $B^1\Sigma^+$  state which is produced in the first two-photon absorption step, is unique in that it exhibits a pronounced double minimum well which results in an extremely broad range of internuclear distances for absorption of the third photon. This allows to also access repulsive Rydberg states which we believe to be the major contributors to the fragmentation channels, while ionization is likely to be due to a combination of direct and autoionization processes.

MO 26.2 Di 16:30 Labsaal

**Trapping and cooling of molecular ions: Towards ultrafast imaging of single molecule structural changes** — ●STEFFEN KAHRA und TOBIAS SCHÄTZ — Max-Planck-Institut für Quantenoptik, Garching

Knowledge about the spacial structure of bio-molecules is a vital prerequisite for a detailed understanding of their functional behaviour in natural environment. In some cases photoexcitation followed by rapid internal structural reorganization of the molecule establishes the basis for ultrafast processes in biology. So far – besides indirect spectroscopic methods dependent on models based on certain theoretic assumptions – there is no technique available to follow these structural changes on the required femtosecond timescale. We propose an experimental scheme using molecular ions in a Paul-trap. Having them sympathetically cooled by ancilla  $\text{Mg}^+$ -ions and aligned by short fs-laser pulses we could benefit from very recent progress in development of short and intense laser sources. They allow the generation of single electron pulses with few fs time resolution. These electrons will be diffracted by the charge density of the isolated molecular ion and thereby leave a measurable signature of its instantaneous structure. For the first time it would be possible to directly observe molecular restructuring by time resolved single electron diffraction on aligned single molecular ions.

## MO 27 Poster: Femtosecond Spectroscopy

Zeit: Dienstag 16:30–18:30

Raum: Labsaal

MO 27.1 Di 16:30 Labsaal

**Shaping of CARS spectra using optimal control theory** — ●S. PEZESHKI, J. LIEBERS, M. SCHREIBER, and U. KLEINEKATHÖFER — Institut für Physik, Technische Universität Chemnitz, 09107 Chemnitz

In experiments it is possible to mode-selectively excite molecules using feedback-controlled shaping of femtosecond laser pulses [1,2]. Here we use the theoretical tool of optimal control [3,4] to influence femtosecond time-resolved coherent anti-Stokes Raman scattering (CARS) signals and spectra. The calculations are done by using time-dependent wave packet calculations together with perturbation theory in the laser field strength. The CARS signals can then be determined using those wave packets of different order in the field strength.

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

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

[3] A. Kaiser and V. May, Chem. Phys. Lett. **405** 339 (2005)

[4] J. Werschnik and E. K. U. Gross, J. Opt. B **7** S300 (2005)

MO 27.2 Di 16:30 Labsaal

**Molecular Decoherence in Solid Environments: Br<sub>2</sub> in solid Ar** — ●MARKUS GÜHR<sup>1,2</sup>, HEIDE IBRAHIM<sup>1</sup>, and NIKOLAUS SCHWENTNER<sup>1</sup> — <sup>1</sup>Institut für Experimentalphysik, Freie Universität Berlin, D-14195 Berlin — <sup>2</sup>Stanford Synchrotron Radiation Laboratory, Menlo Park, California 94025-7015

The intramolecular wave packet dynamics on the electronic B ( $^3\Pi_0$ ) potential of  $\text{Br}_2$  in solid argon is induced and interrogated by femtosecond pump-probe spectroscopy. An effective potential of the chromophore

in the solid is derived from the wave packet period for different excitation photon energies. Deep in the potential well, it is consistent with vibrational energies from wavelength resolved spectra. At higher energies, the vibrational progression merges to a continuum and no potential can be derived from the high resolution spectra. In contrast, the time resolved spectra display pronounced wave packet dynamics which allow to construct an effective potential of the molecule in the matrix, even above the gas phase dissociation limit. This advantage of pump-probe spectroscopy is related to a reduced contribution of homogeneous and inhomogeneous linebroadening. A very large energy loss in the first collision of the molecule with the Ar crystal is observed. This strong interaction with the matrix is directly displayed in an experimental trajectory. Despite the strong energy loss, coherent wave packet oscillations can be observed after the collision. This is attributed to the special symmetry of the molecule-host system.

MO 27.3 Di 16:30 Labsaal

**Ultraschnelle Dynamik eines molekularen Schalters: Fulgide** — •THOMAS BRUST<sup>1</sup>, STEPHAN MALKMUS<sup>1</sup>, SIMONE DRAXLER<sup>1</sup>, CHRISTINE SCHULZ<sup>2</sup>, STEFFEN DIETRICH<sup>2</sup>, KAROLA RÜCK-BRAUN<sup>2</sup>, WOLFGANG ZINTH<sup>1</sup> und MARKUS BRAUN<sup>1</sup> — <sup>1</sup>Ludwig-Maximilians-Universität München, Lehrstuhl für BioMolekulare Optik, Oettingenstr. 67, 80538 München — <sup>2</sup>Technische Universität Berlin, Institut für Chemie, Straße des 17. Juni 124, 10623 Berlin

Reversible molekulare Photo-Schalter, deren Konformationsänderungen durch unterschiedliche Photonenenergien induziert werden, sind interessante Kandidaten für mögliche Anwendungen (optische Speicher, licht-induzierte Konformationsänderungen). Unter diesen photochromen Substanzen zeichnet sich insbesondere die Klasse der Indolylfulgide durch thermodynamische Stabilität ihrer Konformere aus.

Wir untersuchen mittels Femtosekundenspektroskopie die Dynamik dieser Schaltvorgänge, in diesem Fall eine perizyklische Ringschluss- bzw. Ringöffnungsreaktion [1]. Die benötigten Femtosekunden-Lichtimpulse für die beiden Reaktionsrichtungen werden mittels eines selbstgebauten Ti:Sa-basierten Lasersystems und eines nicht-kollinearen optisch parametrischen Verstärkungsprozesses (NOPA) bereitgestellt. Die Reaktionsdynamik wird durch Abtastimpulse im UV/VIS Bereich in einem Anreg-Abtast-Experiment untersucht. Sowohl für die Ringöffnungs- als auch die Ringschlussreaktion werden Zeitkonstanten von unter 10 ps beobachtet. Die Abhängigkeit der Quantenausbeuten von der Temperatur und Anregungswellenlänge wird diskutiert.

[1] S. Malkmus et al., Chem. Phys. Lett. 417 (2005) 266

MO 27.4 Di 16:30 Labsaal

**Molecular tomography: test of accuracy and improvements using time-dependent calculations** — •ELMAR VAN DER ZWAN and MANFRED LEIN — Max-Planck-Institut für Kernphysik, Saupfercheckweg 1, 69117 Heidelberg

Recently a method to perform tomographic imaging of molecular orbitals using High Harmonic Generation (HHG) has been proposed [1]. The method is based on the simplification that the returning electron in the three-step model can be modeled as a plane wave. We investigate the effect of this assumption in a time-dependent calculation by numerically comparing results for the final reconstructed orbital using two different methods which, without the plane-wave assumption, should lead to identical results; namely the reconstruction based on dipole matrix elements or on momentum matrix elements. From this we try to improve on the method. The 3D orbital of a diatomic molecule can be recovered from the 2D projection that results from the tomographic reconstruction. We investigate molecules with anti-symmetric valence orbitals, since these are expected to cause problems in the original scheme.

[1] J. Itatani, J. Levesque, D. Zeidler, H. Niikura, H. Pépin, J.C. Kieffer, P.B. Corkum and D.M. Villeneuve. *Tomographic imaging of molecular orbitals*. Nature 432, 867-871 (2004)

MO 27.5 Di 16:30 Labsaal

**Sub-Picosecond Time-Resolved Infrared Spectroscopy of Phytochrome** — •CHRISTIAN SCHUMANN<sup>1</sup>, RUTH JAKOBER<sup>1</sup>, ROLF DILLER<sup>1</sup>, NORBERT MICHAEL<sup>2</sup>, and TILMAN LAMPARTER<sup>2</sup> — <sup>1</sup>Fachbereich Physik, TU Kaiserslautern, D-67663 Kaiserslautern — <sup>2</sup>Institut für Pflanzenphysiologie, Freie Universität Berlin, D-14195 Berlin

The properties of phytochrome have been subject to numerous investigations, including stationary and low-temperature FTIR, resonance Ra-

man and femtosecond transient absorption spectroscopy in the visible[1].

Here we present the first results of sub-picosecond time-resolved IR vibrational spectroscopy of the primary photoinduced processes of the phytochromes Cph1-PCB and Agp1-BV, which can help elucidate the ultrafast structural dynamics of such systems. The time constant of ca. 16 ps as observed in the band shift dynamics of the chromophore carbonyl stretch vibration indicates a fast chromophore  $P_r$  to  $P_{fr}$  isomerization in Cph1-PCB and is in good agreement with previous results[1].

[1] K. Heyne, J. Herbst, D. Stehlik, B. Esteban, T. Lamparter, J. Hughes and R. Diller; Biophysical Journal 82 (2002), 1004-1016

MO 27.6 Di 16:30 Labsaal

**FS-Study on Bacterial LH1 Complexes: Carotenoid Energy Relaxation Channels** — •PETER GAERTNER<sup>1</sup>, HELMUT PORT<sup>1</sup>, MARCUS BRANSCHAEDEL<sup>2</sup>, and ROBIN GHOSH<sup>2</sup> — <sup>1</sup>3. Physikalisches Institut, Uni Stuttgart — <sup>2</sup>Abteilung Biophysik, Biologisches Institut, Uni Stuttgart

Comperative fs-spectroscopic investigations on light-harvesting 1 (LH1) complexes from mutants of *Rhodospirillum rubrum* (*R.r.*) are reported. The carotenoid chain length effects in LH1 environment are different from carotenoids in solution. The competitive energy relaxation pathways are distinguished upon state-selective photoexcitation.

MO 27.7 Di 16:30 Labsaal

**Trans-cis reaction dynamics in sensory rhodopsin II by femtosecond time-resolved IR spectroscopy: protein and chromophore dynamics** — •RUTH JAKOBER<sup>1</sup>, CHRISTIAN SCHUMANN<sup>1</sup>, ROLF DILLER<sup>1</sup>, JOHANN P. KLARE<sup>2</sup>, and MARTIN ENGELHARD<sup>2</sup> — <sup>1</sup>Fachbereich Physik, Technische Universität Kaiserslautern, 67663 Kaiserslautern — <sup>2</sup>Max-Planck-Institut f. Molekulare Physiologie, 44227 Dortmund

Transient vibrational spectroscopy, which provides insights into processes associated with protein-based photoreactions such as structural changes of the chromophore, its vibrational relaxation and the dynamics of the protein environment, has been performed on sensory rhodopsin II from *Natronomonas pharaonis* at sub-picosecond time resolution.

We present new data on the dynamics of the chromophore and the surrounding protein due to the primary all-trans to 13-cis retinal photoisomerization. Three time constants (0.5 ps, 4 ps and 11 ps) were obtained [1]. It was found that the isomerization takes place within 0.5 ps, followed by an electronic ground state relaxation (4 ps) which corresponds to experiments in the visible spectral region. The 11 ps time constant is discussed as an indication of protein dynamics or a vibrational cooling process.

[1] Rolf Diller, Ruth Jakober, Christian Schumann, Frank Peters, Johann P. Klare, Martin Engelhard; Biopolymers: Biophysics, submitted 2005.

MO 27.8 Di 16:30 Labsaal

**External Electric Field Effects on Ultrafast Electron Transfer Dynamics** — •A.K. SINGH, J. KONRADI, A.V. SCARIA, and A. MATERNY — International University Bremen, Bremen

The ubiquitous nature of electron transfer (ET) reactions has made them a subject of extensive theoretical and experimental research for many decades. However, the number of studies concerning the effect of a static electric field on intramolecular and intermolecular ET processes is limited. An external electric field is expected to influence the rate of the charge separation process considerably in a photo-excited donor-acceptor system through a significant modification of the free energy change ( $\Delta G$ ). Additionally, changes of the electronic coupling between the initial and final states of the ET process have an important influence. Due to a large dipole moment associated with the radical ion pairs produced in the charge separation process,  $\Delta G$  changes in the presence of the external field. As the electron transfer rate is a function of  $\Delta G$ , the reaction dynamics for the production of radical ion pairs is influenced by the introduced perturbation of the system. Depending on the magnitude of the dipole moment and its orientation relative to the electric field, the forward ET rate depends on the applied field. In our contribution, we present results of investigations of the ultrafast ET dynamics under the influence of an external electric field by means of femtosecond time-resolved spectroscopy.

MO 27.9 Di 16:30 Labsaal

**Ultrafast Energy Transfer Between Pigment Molecules Embedded in Mesoporous Cages** — •S. TORK, R.M. RICHARDS, and A. MATERNY — International University Bremen, Bremen

Chlorophylls, along with Carotenoids are crucial pigment molecules involved in light-harvesting processes in photosynthetic organisms. Mimicking the highly efficient energy transfer (ET) systems is a subject of intense investigation to attain the ultimate goal of highly efficient solar energy conversion systems. Considerable efforts have been directed towards the preparation of donor-acceptor (D-A) systems immobilized in various media (*e.g.* films, surfactant micelles, and lipid vesicles). Mesoporous silicas are attractive because of their high surface area, uniform mesopores, and high adsorption capacities. We have synthesized and characterized various mesoporous materials such as MCM (mobile crystalline material) and FSM (folded-sheet mesoporous material) having honeycomb (hexagonal) structures with ordered cylindrical channels of 2–10 nm in diameter. They are potential hosts for the inclusion of bulky organometallic and inorganic complexes and offer nano-scale spaces for the desired arrangement of functional molecules such as chlorophyll. In this contribution, we will present our results on synthesis of mesoporous-chlorophyll-carotenoid compounds and the investigation of the energy transfer process from carotenoids to chlorophylls using femtosecond transient absorption spectroscopy in order to get insight into the energy transfer mechanism.

MO 27.10 Di 16:30 Labsaal

**Considerations for the measurement of the ultrafast heterogeneous electron transfer at metal oxide surfaces using two-photon photoelectron spectroscopy** — ●JODI SZARKO, CHARAF CHERKOUK, LARS GUNDLACH, LIANA SOCACIU-SIEBERT, ANTJE NEUBAUER, RALPH ERNSTORFER, RAINER EICHBERGER, GUIDO MORBACH, and FRANK WILLIG — Hahn-Meitner-Institute, Dept. SE4, Glienicke Str. 100, 14109 Berlin, Germany

The photoinduced electron transfer from organic chromophores into metal oxide surfaces was investigated in our group using time-resolved two-photon photoelectron spectroscopy (2-PPE). A two-color pump-probe technique was made possible by utilizing two nonlinear optical parametric amplifiers (NOPAs) operating at 150 kHz. X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) were also used to characterize the systems. The bare surfaces of the metal oxide crystals were first investigated to determine the best preparation procedure for the optimal surface cleanliness, stoichiometry, and work function for each crystal. The chromophores were then chemically anchored to the surfaces using a wet chemistry technique under inert gas conditions. Finally, the electron injection and transport were determined for the chromophore/metal oxide interfaces.

MO 27.11 Di 16:30 Labsaal

**Dynamics of electron transfer through a chromophore/semiconductor interface** — ●LIANA SOCACIU-SIEBERT, ANTJE NEUBAUER, LARS GUNDLACH, JODI SZARKO, RALPH ERNSTORFER, CHARAF CHERKOUK, GUIDO MORBACH, RAINER EICHBERGER, and FRANK WILLIG — Hahn-Meitner Institut, Abteilung Dynamik von Grenzflächenreaktionen SE4, Glienicke Str. 100, 14109 Berlin, Germany

The ultrafast heterogeneous electron transfer through a chromophore/semiconductor interface was investigated by means of time-resolved two-photon photoemission spectroscopy (TR-2PPE). This pump-probe technique allowed for monitoring simultaneously the time evolution as well as the energy distribution of the injected electrons. The chromophore/semiconductor systems were chosen so that the first excited state of the molecule (donor state) was energetically positioned above the conduction band minimum of the semiconductor. The organic chromophores (perylene derivatives) were chemically anchored on the rutile TiO<sub>2</sub>(110) surface. Different molecular groups, which acts as a bridge, were also inserted between the chromophore and the anchor. The electron transfer rate is strongly influenced by the length and structure of the molecular bridge and, subsequently, the injection times vary over a few orders of magnitude. A systematic study of the dynamics of electron transfer for chromophores with different molecular bridges is presented in this contribution.

MO 27.12 Di 16:30 Labsaal

**Optimal Control of Metal Cluster Reactions by Modulated Ultra-broadband Laser Pulses** — ●BRUNO E. SCHMIDT<sup>1</sup>, DENISIA POPOLAN<sup>1,2</sup>, SANDRA LANG<sup>1,2</sup>, THORSTEN M. BERNHARDT<sup>1,2</sup>, and LUDGER WÖSTE<sup>1</sup> — <sup>1</sup>Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin — <sup>2</sup>Abteilung Oberflächenchemie und Katalyse, Universität Ulm, 89069 Ulm

During the last years the NeNePo technique was applied to study catalytic reaction properties of noble metal cluster-adsorbate complexes in a temperature controlled rf-ion trap. To further innovate this work, we not only aim to analyze the reaction dynamics, but also to steer the reactive system along one desired reaction coordinate and thus to optimize, *e.g.*, the products of a catalytic reaction. To realize this goal, ultra-broadband laser pulses are generated by means of self phase modulation during filamentation process in noble gas atmosphere. Subsequently the broadband pulses are modulated by a liquid crystal mask and irradiated onto the cluster system. The concentration of desired reaction products is optimized in a active feedback loop employing a genetic algorithm. The experimental task is the realization of a broad spectrum which is stable enough to send it to a pulse shaper and to optimize the algorithm for this type of reaction. First results on the spectral properties of the continuum generation relying on self-guiding in noble gas will be presented and its application to the reaction control will be discussed.

## MO 28 Poster: Quantum Control

Zeit: Dienstag 16:30–18:30

Raum: Labsaal

MO 28.1 Di 16:30 Labsaal

**Akkumulative Quantenkontrolle in Nanoliter Flüssigkeitsvolumina** — ●FLORIAN LANGHOJER, FRANK DIMLER und TOBIAS BRIXNER — Physikalisches Institut, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

Bisher übliche adaptive Quantenkontrolltechniken mit geformten Laserimpulsen beruhen auf gleichen Ausgangsbedingungen für jeden neuen Laserimpuls, d.h., jede Wechselwirkung findet mit einem neuen Probenvolumen statt. Um jedoch eine makroskopische Änderung der Probe zu erreichen, ist es auf Grund der meist niedrigen Effizienz nötig, das Photoprodukt zu akkumulieren. Wir stellen einen neuen Aufbau vor, der die Wechselwirkung des Lasers mit kleinsten Flüssigkeitsvolumina (ca. 20 nl) und den schrittweisen Austausch solcher Volumina erlaubt. Die Effekte einer Pulsform auf ein Probenvolumen können so über eine gewisse Zeit akkumuliert und auf Effizienz bzw. erfolgreiche Kontrolle z.B. mit der Pump-Probe Technik evaluiert werden. Dann wird das Probenvolumen gegen ein neues, unbenutztes ausgetauscht. Wir benutzen diese Methode in einer geschlossenen Rückkopplungsschleife. Optimierungen der Pulsform mit einem genetischen Algorithmus benötigen typischerweise weniger als 0.5 ml Probenlösung. Erste Experimente am Laserfarbstoff IR 125 zeigen, dass es möglich ist, ein stabiles Photoprodukt anzuhäufen.

MO 28.2 Di 16:30 Labsaal

**Informationsgehalt der Darstellung ultrakurzer Laserimpulse im Phasenraum** — ●FRANK DIMLER<sup>1</sup>, SUSANNE FECHNER<sup>1</sup>, TOBIAS BRIXNER<sup>1</sup>, GUSTAV GERBER<sup>1</sup> und DAVID J. TANNOR<sup>2</sup> — <sup>1</sup>Physikalisches Institut, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany — <sup>2</sup>Department of Chemical Physics, Weizmann Institute of Science, Rehovot 76100, Israel

Die Repräsentation von ultrakurzen Laserimpulsen im Phasenraum ist ein geeignetes Mittel, sowohl zeitliche als auch spektrale Eigenschaften in einfacher Form darzustellen. Gerade bei den oftmals komplexen Impuls(fol)gen, die im Rahmen der adaptiven Quantenkontrolle erzielt werden, kann eine derartige Repräsentation helfen, die wesentlichen Merkmale zu identifizieren.

Allerdings haben die gebräuchlichen Verteilungsfunktionen nach Wigner oder auch Husimi den Nachteil, dass sie im Vergleich zur herkömmlichen Darstellung des elektrischen Feldes als Intensität und Phase für eine vergleichbare Genauigkeit eine mit dem Quadrat der Anzahl der ursprünglichen Stützstellen skalierende Anzahl an Punkten benötigen.

Zur Reduktion der Information auf das Wesentliche wird die auf einer Arbeit von von Neumann [1] basierende Idee verwendet, dass die minimale Informationseinheit im Phasenraum eine Fläche von  $2\pi\hbar$  ein-



nimmt. In diesem Beitrag werden Untersuchungen dazu vorgestellt und das Verfahren an Beispielen demonstriert.

[1] J. von Neumann, *Math. Ann.* **104**:570-578, (1931)

MO 28.3 Di 16:30 Labsaal

**Post-Tunneling Ionization of Atoms and Molecules in a Mid-IR Laser Field: Dynamics in the Quasistatic Regime** — ●KATHARINE MOORE<sup>1,2</sup>, RYAN COMPTON<sup>2</sup>, DMITRI ROMANOV<sup>3</sup>, and ROBERT LEVIS<sup>2</sup> — <sup>1</sup>Physikalisches Institut, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany — <sup>2</sup>Center for Advanced Photonics Research, Department of Chemistry, Temple University, Philadelphia, PA 19123 USA — <sup>3</sup>Center for Advanced Photonics Research, Department of Physics, Temple University, Philadelphia, PA 19123 USA

Ionization yields are reported for the noble gas Xe and the molecules O<sub>2</sub>, benzene, and *n*-propyl benzene at laser intensities in the range of 10<sup>13</sup>-10<sup>15</sup> W cm<sup>-2</sup> for wavelengths spanning from 800nm to 1600nm. There is an increasing ionization probability in the strong field regime as the excitation wavelength increases from 800nm to 1600 nm at fixed field intensity. The measured thresholds for the ionization event scale approximately as  $\lambda^{-2}$ . These observations are counter-intuitive from either the multiphoton or tunneling perspective. A simple quantitative model is developed that extends through-the-barrier tunneling with single photon ionization from a Rydberg intermediate state and captures the wavelength dependence.

MO 28.4 Di 16:30 Labsaal

**Dynamical freezing of molecular alignment.** — ●A. MATOS-ABIAGUE, A. S. MOSKALENKO, and J. BERAKDAR — Max-Planck Institut für Mikrostrukturphysik, Weinberg 2, 06120 Halle, Germany.

The sustainability in time of the alignment of diatomic molecules driven by periodic trains of short laser pulses is investigated. From an analysis of the geometry of quantum evolution we deduce necessary and sufficient conditions for dynamically freezing the time evolution of the system. Once dynamical freezing is reached, an initially aligned molecule remains well aligned for a time of the order of the duration of the complete train of pulses. The inferred necessary and sufficient conditions governing the dynamical freezing are then used for obtaining the field parameters capable of sustaining the molecular alignment. By performing a numerical simulation of the alignment of iodine monochloride molecules subject to a train of laser pulses we demonstrate that the appropriate designing of the external time-dependent field leads, indeed, to a strong, time sustainability of the molecular alignment.

MO 28.5 Di 16:30 Labsaal

**Optimale Kontrolle der Photoisomerisierung von Bakteriorhodopsin** — ●DANIEL WOLPERT, GERHARD VOGT, PATRICK NUERNBERGER, TOBIAS BRIXNER und GUSTAV GERBER — Physikalisches Institut, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

Wir untersuchen die Steuerung der Photoisomerisierungsreaktion von Retinal im Transmembranprotein Bakteriorhodopsin. Bestrahlung mit sichtbarem Licht setzt einen Photozyklus in Gang, an dessen Anfang das Retinal vom *all-trans* in den *13-cis* Zustand gebracht wird. Adaptive Femtosekundenpulsformung wird verwendet, um die Effizienz der Isome-

risierungsreaktion zu verändern. Das Retinalmolekül wird mit phasen- und amplitudengeformten Femtosekundenlaserimpulsen angeregt. Um die optimale Impulsform zu finden, wird ein evolutionärer Algorithmus mit Rückkopplung aus einem transienten Absorptionssignal, das charakteristisch für das *cis* Photoprodukt ist, benutzt. Mit diesem Schema kann das Verhältnis zwischen *cis*- und *trans*-Isomer optimal kontrolliert werden. Zusätzlich wurde ein Kontrollschema mit drei Impulsen (pump-dump-probe) verwendet, wobei der dump-Impuls phasenmoduliert ist. Dies eröffnet die Möglichkeit, das Wellenpaket in der Nähe der konischen Durchscheidung zu beeinflussen.

MO 28.6 Di 16:30 Labsaal

**Single-beam CARS Microscopy employing Coherent Control Schemes** — ●B. VON VACANO, W. WOHLLEBEN, and M. MOTZKUS — Physikalische Chemie, Philipps-Universität, 35032 Marburg

Nonlinear Raman scattering allows spectroscopic characterization of samples with microscopic spatial resolution. CARS (Coherent Anti-Stokes Raman Scattering) is a nonlinear four-wave-mixing process, revealing the vibrational structure of molecular samples. Due to the non-linearity of the process, the signal generation can be confined to a microscopic volume allowing chemical imaging. Single-beam CARS accomplishes a complete CARS scheme with tailored fs-pulses from one single broadband laser source by coherent control of the nonlinear signal generation [1].

Here, we compare different schemes for single-beam CARS. We present a single-beam approach for truly time resolved CARS spectroscopy [2] and discuss the applicability of single-beam CARS schemes for microscopic imaging.

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

[2] B. von Vacano, M. Motzkus. *Optics Communications*, submitted.

MO 28.7 Di 16:30 Labsaal

**Quantum control spectroscopy in biomolecules** — ●TIAGO BUCKUP, WENDEL WOHLLEBEN, TIMO LEBOLD, ALEXANDER WEIGEL, and MARCUS MOTZKUS — Physikalische Chemie, Phillips Universität Marburg, 35043 Marburg, Germany

Biomolecules present very often complex energy deactivation networks with overlapping electronic absorption bands, which makes their study a difficult task. This can be specially true in transient absorption spectroscopy. However, quantum control techniques can be used to discriminate specific electronic states of interest by optimizing one, two or more photon transitions. Recently, we have shown the control of energy flow in the bacterial light-harvesting using shaped pump pulses in the visible and the selective population of different pathways in  $\beta$ -carotene using an additional depletion pulse in the transient absorption technique. Here, we make one step further and apply a closed-loop optimization setup to a prototype molecule ( $\beta$ -carotene) using a spatial light modulator to decipher the energy flow network after a multiphoton excitation with an ultrashort pulse in the near-IR. After excitation, two overlapping bands were detected and identified as the S<sub>1</sub> state and the first triplet state T<sub>1</sub>. Using as feedback the transient absorption signal at a specific probe delay, the triplet signal could be optimized over the singlet contribution.

## MO 29 Poster: Biomolecules

Zeit: Dienstag 16:30–18:30

Raum: Labsaal

MO 29.1 Di 16:30 Labsaal

**Site selectivity in dissociative free-electron attachment to gas phase nucleobases** — ●SYLWIA PTASINSKA<sup>1</sup>, STEPHAN DENIFL<sup>1</sup>, FABIO ZAPPA<sup>1,2</sup>, VERENA GRILL<sup>1</sup>, PAUL SCHEIER<sup>1</sup>, and TILMANN D. MÄRK<sup>1</sup> — <sup>1</sup>Institut für Ionenphysik, Leopold-Franzens Universität Innsbruck, Technikerstr. 25, A-6020 Innsbruck, Austria — <sup>2</sup>UNESA, Rio de Janeiro, Brasil

The interaction of low energy electrons with DNA has been demonstrated to be an important mechanism in the production of both single and double strand breaks, even at sub-ionization energies [1]. Furthermore, the yield of such DNA damage shows a resonant behaviour with energy which is an indication of transient negative ion formation. In this contribution we will show the results of a series of gas phase experiments concerning free-electron attachment to the nucleobases thymine and uracil and partially deuterated or methylated derivatives. By care-

ful analysis of the experimental data, we are able to assign each of the resonances of the abundant fragment anions (M-H)<sup>-</sup> and H<sup>-</sup> observed to the cleavage of an H atom from a specific site in these molecules.

This work was supported by FWF (Wien), the EU commission (Brussels, through the EPIC network and the COST Action P9). F.Z gratefully acknowledges a post-doc grant from the Brazilian agency CNPq.

[1] M. A. Huels, B. Boudaiffa, P. Cloutier, D. Hunting, L. Sanche, J. Am. Chem. Soc. **125**(2003) 4467;

MO 29.2 Di 16:30 Labsaal

**Stability of uracil and thymine cations** — ●MANUEL BEKIRCHER<sup>1</sup>, SYLWIA PTASINSKA<sup>1</sup>, STEFAN FEIL<sup>1</sup>, MANUEL WINKLER<sup>1</sup>, ARNTRAUD BACHER<sup>1</sup>, WERNER SCHUSTEREDER<sup>2</sup>, STEPHAN DENIFL<sup>1</sup>, OLOF ECHT<sup>3</sup>, TILMANN D. MÄRK<sup>1</sup>, and PAUL SCHEIER<sup>1</sup> — <sup>1</sup>Institut für Ionenphysik, Universität Innsbruck, Technikerstrasse 25, 6020 Innsbruck, Austria — <sup>2</sup>Max-Planck-Institut für Plasmaphysik, D-85748 Garching, Germany — <sup>3</sup>Department of Physics, University of New Hampshire, Durham, USA

Attachment of free electrons to uracil and thymine leads exclusively to the formation of fragment anions and the most abundant product are (U-H)- and (T-H)-, respectively [1]. However, in the positive mass spectrum of these molecules no H-loss is observed. This is in contrast to electron im-

pact ionization of hydrocarbons where H-loss is an important process. In the present study H-loss from excited uracil cations has been discovered and the resulting ion (U-H)<sup>+</sup> is observed to decay quickly into more stable products upon ring dissociation. The measurements are performed utilizing a modified VG-ZAB mass spectrometer in reversed geometry. The uracil and thymine molecules are ionized by electron impact at 74 eV. The ions are then accelerated at different acceleration voltages, from 1 to 10 kV, resulting in different flight times to the detector. By decoupling the two sector fields single decay processes are studied in two different windows and even the sequential decay of metastable uracil can unambiguously be identified.

[1] S. Denifl, S. Ptasinska, M. Probst, J. Hrusak, P. Scheier and T.D. Märk, *J. Phys. Chem. A* 108 (2004) 6562-6569

## MO 30 Poster: Quantum Chemistry

Zeit: Dienstag 16:30–18:30

Raum: Labsaal

MO 30.1 Di 16:30 Labsaal

**Use of double group theory for analyzing the term splitting in crystal fields** — ●KATYA RYKHLINSKAYA and STEPHAN FRITZSCHE — Universität Kassel, Institut für Physik, D-34132 Kassel, Germany

The electron structure and symmetry of crystals can be resolved by investigating the term splitting of atoms in a crystal field. i. e. if the electron density of the atom has to obey the symmetry of the crystal. Then, the presence of the electron spin and the spin-orbit interaction leads to an additional term splitting [1]. In fact, the concept of spin is very important to explain a number of phenomena, such as electron paramagnetic resonance, the Zeeman effect and various others.

The splitting of the electron terms in a crystal field can be treated using the so-called double symmetry groups. To facilitate the use of the double group theory we present the program BETHE [2], which has been extended recently in order to classify the term splitting in crystal fields and to generate approximate wave functions for atomic levels. In addition, our program also provides a simple access to the group theoretical data for 72 most widely applied point and double groups. The interactive design of this program is illustrated by a number of examples which may help the user in following the literature and in daily research work.

[1] B. S. Tsukerblat, *Group Theory in Chemistry and Spectroscopy* (Academic Press, London, 1994).

[2] K. Rykhlinskaya, S. Fritzsche, *Comp. Phys. Commun.*, 171 (2005) 119.

MO 30.2 Di 16:30 Labsaal

**Berechnung der magnetischen Eigenschaften kleiner Moleküle und Cluster in Rahmen der nicht-kollinearen DFT** — ●J. ANTON und B. FRICKE — Institut für Physik, Universität Kassel, 34109 Kassel

Bei der Berechnung spektroskopischer Eigenschaften von kleinen Molekülen und Clustern wird oft die Dichte-Funktional-Theorie verwendet. Die Güte solcher Rechnungen hängt entscheidend von den verwendeten Austausch-Korrelation-Funktionalen ab. Für die offen-schaligen Moleküle ist es zB. notwendig die Spin-Polarisation der Elektronenhülle zu berücksichtigen. In einer nicht-relativistischen Beschreibung werden dann Dichte-Funktionale verwendet, die nicht von der Ladungsdichte sondern von der Spin-Dichten abhängen. Bekanntlich ist der Spin eines Teilchen in einer relativistischen Beschreibung keine gute Quantenzahl, so daß dieses Konzept in die relativistische Theorie nicht übernommen werden kann. Dieses konzeptionelle Problem läßt sich aber mit Hilfe der Magnetisierungsdichte umgehen. In den letzten Jahren haben wir unseres relativistische DFT-Programm um die Magnetisierungsdichte erweitert [1]. Dies hat nicht nur zu deutlichen Verbesserungen bei der Berechnung der spektroskopischen Eigenschaften geführt, sondern öffnete uns zusätzlich einen Zugang zu den magnetischen Eigenschaften von Molekülen und Clustern.

Es werden die Auswirkungen der Nicht-Kollinearität der Magnetisierungsdichte auf die spektroskopischen und magnetischen Eigenschaften kleiner Moleküle und Cluster diskutiert. Diese Ergebnisse werden auch

mit den experimentellen Werten verglichen.

[1] J. Anton, B. Fricke, E. Engel, *Phys. Rev. A* 69, 012505 (2004)

MO 30.3 Di 16:30 Labsaal

**Classical calculation of transient absorption spectra monitoring ultrafast electron transfer processes** — ●IGOR USPENSKIY, BIRGIT STRODEL, and GERHARD STOCK — Institut für Physikalische und Theoretische Chemie, J.W. Goethe Universität Marie-Curie-Str. 11, 60439 Frankfurt am Main, Germany

The mapping approach [1] is applied to the classical description of the ultrafast electron transfer processes. Several classical approximations to calculate time- frequency- resolved pump-probe spectra are represented. We generalize various versions of semiclassical Frank-Condon approximation to the case of nonadiabatically coupled potential energy surfaces [2]. Moreover, we employed classical electron analog model to define the classical analog of electron dipole transition operator [3]. We studied foregoing methods for models, which describe (i) the internal conversions in symmetric potential spin-boson model with external ground state, and (ii) electron-transfer model in mixed-valence system of the compound (NH<sub>3</sub>)<sub>5</sub>Ru<sup>III</sup>NCRu<sup>II</sup>(CN)<sub>5</sub><sup>-</sup> with reduced number of vibrational modes. Exact reference data are compared to approximate calculations of populations, wave-packet motions, as well as time-frequency resolved spectra for various durations of the pump and probe pulses.

[1] G. Stock and M. Thoss, *Phys. Rev. Lett.* 78, 578 (1997).

[2] S. Diltthey, S. Hahn, and G. Stock, *J. Chem. Phys.* 112, 4910 (2000).

[3] G. Stock and W. H. Miller, *J. Chem. Phys.* 99, 1545 (1993).

MO 30.4 Di 16:30 Labsaal

**Quantum-classical calculation of time-resolved infrared spectra of biomolecules** — ●ROMAN GORBUNOV, NGUYEN PHUONG, and GERHARD STOCK — Institut für Physikalische und Theoretische Chemie, J.W. Goethe Universität, Marie-Curie-Str. 11, 60439 Frankfurt am Main, Germany

Various approaches for the calculation of vibrational spectra of peptides in aqueous solution are discussed. To describe the amide I vibrations in peptides, we use an ab initio based exciton model combined with a solvent correction of local amide I frequencies. The exciton model of amide I vibrations contains the conformationally dependent force constants of the local vibrations as well as the coupling between them. The solvent correction is based on an empirical relation between frequency of the local vibrations in peptide and the corresponding electric field produced by surrounding water molecules. Conformational dynamics of the peptide and the dynamics of surrounding water molecules were obtained by classical molecular dynamic simulations. In the present work, we have studied the influence of the solvent correction on the vibrational spectra. Different protonation states (reflecting different pH values) were considered and their influence on the vibrational spectra was investigated. The accuracy of the second order cumulant expansion and the Condon approximation were studied for different cases.

## MO 31 Poster: Molecular Dynamics

Zeit: Dienstag 16:30–18:30

Raum: Labsaal

MO 31.1 Di 16:30 Labsaal

**Numerical Examination of Beyond-Born-Oppenheimer Dynamics in the Hydrogen Molecular Ion** — ●STEFAN PIEPER and MANFRED LEIN — Max-Planck-Institute for Nuclear Physics, Heidelberg

An  $\text{H}_2^+$  molecular ion (1+1 D) is exposed to a short intense laser pulse. The time dependent Schrödinger Equation is solved numerically on a 2D grid that is split into an inner and outer part. For large values of the electronic coordinate, the wave function is decomposed in products of electronic and nuclear wave functions, and the electron is assumed to move in a fixed effective potential, so that the two degrees of freedom can be treated independently. As a consequence, the numerical effort is significantly reduced and the electronic grid can be larger than  $10^4$  a.u. This enables one to keep the full wave function on the grid, even for pulses long enough to allow for substantial nuclear motion, and to examine kinetic-energy spectra of both the nuclei and the electron without loss of probability. In our approach we allow for wave packets being transferred in both directions between inner and outer region.

The 1D Coulomb interaction is modified beyond the usual soft core potential to account for the real motion of the electron in three dimensions, i.e. the Born-Oppenheimer potentials are reproduced more accurately for the two lowest lying states.

MO 31.2 Di 16:30 Labsaal

**Nonlinear time series analysis of peptide dynamics** — ●RAINER HEGGER, ALEXANDROS ALTIS, and GERHARD STOCK — J.W. Goethe Universität, Institut f. Physikalische und Theoretische Chemie, Marie-Curie Str. 11, 60439 Frankfurt

During the last few years the computer simulation of peptide dynamics has become feasible, by using an all-atom force field and an explicit or implicit representation of the solvent. Since the simulations produce a huge amount of data, it is of great importance to develop and improve suitable tools to analyze and interpret these data. As a new approach to this well-known problem, we suggest to apply the ideas originating from the theory of nonlinear dynamical systems to analyze molecular dynamics data. The goal is to develop mathematical models which, on one hand, are simple enough to be analyzed in great detail, and on the other hand, are realistic enough to reproduce the essential features of the dynamics.

In this work we present results obtained for small peptides ( $\leq 10$  amino acids). By performing a PCA rotation in the space spanned by the dihedral angles of the peptide, we get rid of the dominant linear correlations between the peptide degrees of freedom. In the new coordinate system we are able to reveal the leading nonlinear properties.

By means of an analysis of these nonlinear properties we are able to describe the chaoticity of the system as a function of molecular properties, such as the length, the sequence and the types of residues of the peptide and thereby we obtain novel insight into the complexity and cooperativity of peptide folding.

## MO 41 Hauptvorträge

Zeit: Mittwoch 10:40–12:40

Raum: H12

**Hauptvortrag**

MO 41.1 Mi 10:40 H12

**Light and molecules: from structure to function using laser pulses** — ●LETICIA GONZÁLEZ — Institut für Chemie und Biochemie, Takustrasse 3, 14195 Berlin

This talk will address the problem of tracking the ultrafast dynamics of light induced reactions in real time and its possible manipulation from the theoretical point of view. The different steps that take place in a chemical reaction, like breaking and forming of bonds, isomerization processes, etc, occur in a femtosecond time regime. Using laser pulses in this time scale, it is possible to follow carefully the movement of the nuclei. Furthermore, today's laser technology has made it possible to shape laser pulses in such a way that a particular nuclear motion can be artificially imprinted, leading to the so-called coherent control of molecular reactions. Using quantum chemistry and wave packet propagations I will illustrate how to use laser light to maneuver the structure and function of polyatomic systems. Specifically, molecular orientation, selective dissociation of molecular bonds, how to separate enantiomers from a racemic mixture, and how to initiate a molecular rotor will be shown.

**Hauptvortrag**

MO 41.2 Mi 11:10 H12

**Ultrafast bimolecular proton transfer in water: from direct exchange to sequential hopping** — ●ERIK T. J. NIBBERING<sup>1</sup>, OMAR F. MOHAMMED<sup>1</sup>, JENS DREYER<sup>1</sup>, DINA PINES<sup>2</sup>, and EHUD PINES<sup>2</sup> — <sup>1</sup>Max Born Institut für Nichtlineare Optik und Kurzzeitspektroskopie, D-12489 Berlin, Germany — <sup>2</sup>Department of Chemistry, Ben Gurion University of the Negev, Beersheva 84125, Israel

Bimolecular acid-base neutralization reactions in aqueous solution involve, according to Eigen and Weller, diffusive motion, and upon formation of the reactive encounter complex, an exchange of a proton. Until now the nature of this encounter pair had not been elucidated. Proton transfer may occur in a tight complex between acid and base directly bound by a hydrogen bond, forming the reaction coordinate. An encounter complex may also involve an acid and base connected via a water bridge [1]. We now have been able to determine the ultrafast proton transfer rates of these tight and loose acid-base complexes with femtosecond infrared spectroscopy. We use the dye stain pyranine as optically triggered acid (photoacid ROH) as a means to follow in real time its reaction with carboxylic bases B<sup>-</sup>. By monitoring infrared-active marker modes we are

able, in the case of the loose complexes, to follow the sequential, von Grothuss type, hopping of the proton from the photoacid, through an intermediate water bridge, to the base [2]. The transient spectra of the hydrated proton band indicate a hydronium cation  $\text{H}_3\text{O}^+$  stabilized in an Eigen configuration in an ionic complex  $\text{RO}^- \cdots \text{H}_3\text{O}^+ \cdots \text{B}^-$ . [1]. M. Rini et al., Science 301, 349 (2003); J. Chem. Phys. 121, 9593 (2004). [2]. O. F. Mohammed et al., Science 310, 83 (2005).

**Hauptvortrag**

MO 41.3 Mi 11:40 H12

***o*-Nitrobenzaldehyde: A "Tool" to study Hydrogen Transfer Reactions, Nucleophilic Additions, and Eliminations** — ●PETER GILCH, HILMAR SCHACHENMAYR, WOLFGANG SCHREIER, and STEFAN LAIMGRUBER — Department für Physik, Ludwig-Maximilians-Universität, Oettingenstr. 67, D-80538 München, Germany

Upon light absorption *o*-nitrobenzaldehyde is transformed into *o*-nitrosobenzoic acid. Although this reaction has first been described more than 100 years ago it is only now that by femtosecond vibrational spectroscopy intermediates of this reaction have been unequivocally identified [1]. The excitation of NBA initiates a hydrogen transfer which within 400 fs results in the formation of a first ground state intermediate - a ketene. This ketene has been observed via femtosecond IR spectroscopy. The ketene is subject to a nucleophilic addition occurring with a strongly solvent dependent reaction time (with time constants of  $\sim 10$  ps – 2 ns). In protic solvents the reaction takes place while the ketene is still vibrationally hot which results in non-exponential kinetics. The product of the addition is characterized by IR and stimulated Raman spectroscopy. It transforms into the final nitroso product via an elimination. Thus, NBA allows to study at least three elementary reaction types of organic chemistry.

[1] S. Laimgruber et al., Angew. Chem. Int. Ed. 44 (2005) 7901.

**Hauptvortrag**

MO 41.4 Mi 12:10 H12

**Peptides and peptide aggregates in the gas phase: what do we learn from isomer selective IR/UV spectroscopy** — ●MARKUS GERHARDS — H.-Heine Universität Düsseldorf, Institut für Physikalische Chemie I, Universitätsstraße 26.33.02, 40225 Düsseldorf

Secondary structures play an important role to explain the function of proteins. There are different important binding motifs like  $\beta$ -sheets,

$\alpha$ -helices,  $\beta$ -turns or  $\gamma$ -turns. These structures are stabilized by intra- or intermolecular hydrogen bonds. In order to figure out the influence on structure and individual hydrogen bonds upon aggregation with water and to learn more about the driving forces to form secondary structures, isolated di- up to pentapeptides and peptide aggregates are analyzed by mass-, isomer-, and state-selective combined IR/UV techniques, i.e. for each isomer of a given peptide the individual IR spectrum can be recorded in a molecular beam experiment. In combination with force field

and ab initio calculations the IR spectra yield the structural binding motif and the strength of the hydrogen bonds. By adding water gradually the influence of a microsolvation shell on the secondary structure can be investigated. Not only water but also templates can form aggregates with peptides. The chosen templates are important to inhibit pathogenic  $\beta$ -sheets, especially the aggregation of templates to a peptide sequence responsible for Alzheimer disease will be discussed.

## MO 42 Excitation and Coherence Decay

Zeit: Mittwoch 14:00–16:00

Raum: H12

MO 42.1 Mi 14:00 H12

**Photoinduced multielectron dynamics in large finite systems: A two-color pump-probe mass-spectroscopic study on C<sub>60</sub>** — ●I. SHCHATSININ, T. LAARMANN, A. STALMASHONAK, N. ZHAVORONKOV, C. P. SCHULZ, and I. V. HERTEL — Max-Born-Institute, Max-Born Str. 2a, D-12489 Berlin, Germany

C<sub>60</sub> fullerenes may be seen as a prototype of a large, finite system for investigations of the electronic and nuclear responses in strong laser field [1]. We have studied the ionization and fragmentation dynamics of C<sub>60</sub> with time-resolved, two-color, pump-probe spectroscopy using sub-30-fs pulses of 400 nm (pump) and 800 nm (probe) wavelength. The recorded signals of mother ions and fragments as a function of the delay time between pump and probe pulses and as a function of their laser intensities ( $5 \times 10^{12}$ – $1 \times 10^{14}$  Wcm<sup>-2</sup>) contain information on the energy redistribution within the molecule. The resonant pre-excitation of the "t<sub>1u</sub>-doorway" state by a weak, blue pulse results in a significant enhancement of highly charged mother ions and fragments by the strong, delayed probe pulse. The observed ultrafast dynamics will be discussed in the picture of nonadiabatic multi-electron dynamics (NMED) which is currently of great interest.

[1] I. V. Hertel, T. Laarmann, and C. P. Schulz, *Ad. At. Mol. and Opt. Phys.* 50, 219 (2005)

MO 42.2 Mi 14:15 H12

**Femtosecond time resolved Experiments on the *t*-Butyl Radical** — ●BASTIAN NOLLER<sup>1</sup>, LIONEL POISSON<sup>2</sup>, RAMAN MAKSIMENKA<sup>1</sup> und INGO FISCHER<sup>1</sup> — <sup>1</sup>Institut für Physikalische Chemie, Universität Würzburg, Am Hubland D-97074 — <sup>2</sup>CEA Saclay, Bâtiment 522, 91191 Gif sur Yvette

The photophysics of the 3s and 3p state of the *t*-Butyl radical, C<sub>4</sub>H<sub>9</sub>, were investigated by femtosecond time resolved pump probe experiments in the gas phase. The radicals were produced by flash pyrolysis of Azot-*t*-butane. Three detection methods were used to elucidate the dynamics of the radical: Time of flight mass spectroscopy, photoion imaging and photoelectron imaging. Interestingly the lifetime of the 3 <sup>2</sup>A<sub>1</sub> (3p) state at 255 nm is longer than the lifetime of the lower lying 2 <sup>2</sup>A<sub>1</sub> (3s) state at 330 nm (1.9 ps vs. 110 fs).

MO 42.3 Mi 14:30 H12

**Xanthone in Water — Fast Intersystem Crossing and Intense Fluorescence** — ●BJÖRN HEINZ<sup>1</sup>, BERNHARD SCHMIDT<sup>1</sup>, CHRISTOPHER ROOT<sup>1</sup>, HELMUT SATZGER<sup>1</sup>, FRANZ MILOTA<sup>2</sup>, BEAT FIERZ<sup>3</sup>, THOMAS KIEFHABER<sup>3</sup>, WOLFGANG ZINTH<sup>1</sup>, and PETER GILCH<sup>1</sup> — <sup>1</sup>Department für Physik, Ludwig-Maximilians-Universität, Oettingenstr. 67, D-80538 München, Germany — <sup>2</sup>Institut für Physikalische Chemie der Universität Wien, Währingerstraße 42, A-1090 Wien, Austria — <sup>3</sup>Division of Biophysical Chemistry, Biozentrum, University of Basel, Klingelbergstraße 50/70, CH-4056 Basel, Switzerland

Due to their efficient intersystem crossing (ISC) aromatic carbonyl compounds are of great importance in photophysics and photochemistry. They, for instance, serve as triplet sensitizers and thereby allow to access triplet states of molecules with low inherent ISC yields. Because of its rigid and symmetric structure the carbonyl compound xanthone has been thoroughly studied by various spectroscopic techniques. In most solvents (non-polar and polar) the fluorescence quantum yield is very low ( $\sim 10^{-4}$ ) in accordance with short ISC times. In water this yield is as high as 0.05. Still, a fast ISC process is observed. We propose a delayed fluorescence scheme to account for these observations. The scheme will be underscored by time resolved fluorescence and absorption measurements. The scheme allows to extract energetic information on the triplet states not accessible heretofore.

MO 42.4 Mi 14:45 H12

**Molecular mechanisms of fluorescence quenching of organic pigments** — ●LISA LORENZ, VICTOR MATYLITSKY, KARSTEN NEUMANN, and JOSEF WACHTVEITL — J.W. Goethe Universität, IPTC, Marie-Curie-Str. 11, 60439 Frankfurt/Main

The occurrence of fluorescence of crystalline pigments is often explained by their intermolecular distance, which is thought to be the main parameter determining fluorescence quenching. In a recent study of the organic pigment P.Y.101 we found that in contradiction to common rules for solid state fluorescence, the radiationless deactivation of the excited state is a property of the individual molecule rather than a cooperative one.

In time resolved experiments on P.Y. 101 and three of its derivatives (one fluorescent and two non-fluorescent di-naphthyl-bisazomethin-based pigments), which are very similar in structure, we were able to show the dynamics and reaction pathways of deactivation. By embedding P.Y. 101 in a polyethylene matrix it was possible to compare dynamics in solution and in the microcrystalline state. It was found that the dynamics are slowed down by a factor of four in the solid state. For the non-fluorescent pigments a long-lived intermediate was observed which decays via internal conversion.

These results are in excellent agreement with time-dependent DFT[1,2] studies of the excited state properties of P.Y. 101 and its derivatives.

1.) A. Dreuw et al. *Angew. Chem. Int. Ed.*, 44, 7783, 2005

2.) J. Ploetner and A. Dreuw Solid-state fluorescence of Pigment Yellow 101 and derivatives: a conserved property of the individual molecules *Phys. Chem. Chem. Phys.*, 2006, in press

MO 42.5 Mi 15:00 H12

**Anisotropie nicht entarteter und (quasi)-entarteter Systeme - dynamische und statische Eigenschaften** — ●OLIVER SCHALK und ANDREAS-NEIL UNTERREINER — Universität Karlsruhe (TH), Lehrstuhl für Molekulare Physikalische Chemie, Kaiserstr. 12, 76128 Karlsruhe

Die transiente Anisotropie ist eine wichtige Methode der Ultrakurzzeitspektroskopie zur Charakterisierung von Moleküleigenschaften. Sie liefert u. a. Informationen über die Rotationsbewegung von Molekülen in flüssiger und gasförmiger Phase. Eine wichtige Größe ist dabei die Anisotropie zum Zeitpunkt  $t = 0$  (Anfangsanisotropie). Es ist bekannt, dass dieser Wert im Falle zweier elektronisch entarteter, angeregter Zustände den Wert 0,7 erreichen kann - im Gegensatz zu 0,4 für einen nichtentarteten Zustand. Gänzlich unbekannt ist jedoch das Verhalten bei quasi-entarteten Zuständen. Ein von uns weiterentwickeltes Modell kann sowohl die Rotationsdynamik als auch die Dynamik in Systemen mit entarteten angeregten Zuständen beschreiben. Ferner erhält man neue Erkenntnisse bzgl. des bekannten gaußförmigen Abklingens der Anisotropie durch Rotation sowie der Multiphotonenspektroskopie und der Dynamik im entarteten System. Eine Beschreibung der Anfangsanisotropie eines Systems mit quasi-entarteten Zuständen ist ebenfalls möglich. Als Anwendungsbeispiel dient Cycloheptatrien, welches eine unerwartet hohe Anfangsanisotropie von etwa 0,6 zeigt, was als quasi-Entartung zweier Zustände gedeutet werden kann, die z.B. über eine konische Überschneidung gekoppelt sein können.

MO 42.6 Mi 15:15 H12

**Ultrafast proton transfer and vibrational coherence in the gas phase** — ●CHRISTIAN SCHRIEVER, STEFAN LOCHBRUNNER, and EBERHARD RIEDLE — LS für BioMolekulare Optik, Ludwig-Maximilians-Universität München

The ultrafast excited state intramolecular proton transfer (ESIPT) is a prototype photoinduced chemical reaction that strongly couples electronic and nuclear motion. It has recently been studied by means of

transient absorption measurements with sub-30-fs resolution. From these measurements a novel model of the ESIPT mechanism was derived that emphasizes the importance of the slow skeletal modes [1]. Typically, the wavepackets that are observed in the keto form after the ESIPT dephase on a time scale of 1 ps. It is not yet known whether this dephasing is mainly due to intramolecular vibrational coupling or due to the influence of the solvent. Neither is it known, whether the ESIPT and its irreversible nature depend on the solvent for a given molecule. We will decide these questions by comparison of the solution phase and the gas phase ultrafast behavior. The measurement in the gas phase is quite challenging due to the low vapor pressure that necessitates a collinear pump probe arrangement with matching of the beam sizes over a long range. To maximize the transient signal, we have recorded time resolved spectra from 310 to 700 nm. These reveal very large absorptions in the near UV that render a fivefold larger signal than the stimulated emission in the visible.

[1] S. Lochbrunner, A. J. Wurzer, and E. Riedle *J.Phys.Chem. A* **107**, 10580 (2003)

MO 42.7 Mi 15:30 H12

**Quantum interference oscillations of fs-photoionization of heavy alkali-doped Helium nanodroplets** — ●MARCEL MUDRICH<sup>1</sup>, OLIVER BÜNERMANN<sup>1</sup>, GEORG DROPELMANN<sup>2</sup>, PATRICK CLAAS<sup>2</sup>, CLAU-PETER SCHULZ<sup>3</sup>, and FRANK STIENKEMEIER<sup>1</sup> — <sup>1</sup>Physikalisches Institut, Universität Freiburg — <sup>2</sup>Physikalische Fakultät, Universität Bielefeld — <sup>3</sup>Max-Born-Institut, Berlin

Quantum interference (QI) oscillations of the ion yield obtained from fs pump-probe photoionization of K, Rb, and Cs attached to He nanodroplets are recorded. All three heavy alkalis are found to form alkali-helium exciplexes which also show QI [1,2,3]. The observation of QI of RbHe photoionization over tens of picoseconds demonstrates that laser induced coherence persists even when a new molecular bond is formed. Analysis of the QI frequency spectrum allows to determine the vibrational level structure of the exciplex molecule. Moreover, the change in vibrational energies and vibrational cooling can be followed in real time during exciplex formation.

[1] C.P. Schulz, P. Claas and F. Stienkemeier, *Phys. Rev. Lett.* **87**, 153401 (2001)

[2] G. Droppelmann, O. Bünermann, C.P. Schulz, and F. Stienkemeier, *Phys. Rev. Lett.* **93**, 023402 (2004)

[3] O. Bünermann, M. Mudrich, M. Weidemüller, and F. Stienkemeier, *J. Chem. Phys.* **121**, 8880 (2004)

MO 42.8 Mi 15:45 H12

**Vibrational relaxation and wavepacket motion in electronically excited perylene dyes in solution** — ●PATRIZIA KROK, IDA Z. KOZMA, STEFAN LOCHBRUNNER, and EBERHARD RIEDLE — LS für BioMolekulare Optik, Ludwig-Maximilians-Universität München

We study the S<sub>1</sub> state vibrational dynamics of perylenbisimid dyes in solution. The absorption spectrum and the emission spectrum show a well structured progression that is mainly due to a single vibration. By selective excitation of the first three vibronic levels and probing at suitable wavelengths, we find a time constant of about 2 ps for the vibrational reorganization in the nonyldecyl bisubstituted dye S-19. We attribute this time constant to internal vibrational redistribution as well as relaxation to the solvent, i.e. the population decay of the optically excited vibrational level.

A complementary experiment investigates the ultrafast wavepacket motion in S-19 and related dyes to identify the Franck-Condon active modes and their dephasing and decay mechanism. We create a superposition of vibronic states with spectrally broad 11-fs pulses at 510 nm and detect oscillations at about 500, 1300 and 1500 cm<sup>-1</sup> with 10-fs probe pulses centered in the emission region. The vibrational frequencies are compared to calculations and measurements in helium nano droplets [1]. The decay of the wavepacket motion allows us for the first time to decide whether pure vibrational dephasing is a significant contribution in addition to the population decay.

[1] M. Wewer and F. Stienkemeier, *Phys.Chem.Chem.Pys.* **7**, 1171 (2005)

## MO 43 Biomolecules I

Zeit: Mittwoch 14:00–16:00

MO 43.1 Mi 14:00 H10

**Rotationally resolved electronic spectroscopy of biomolecular building blocks** — ●MICHAEL SCHMITT, MARCEL BÖHM, CHRISTIAN RATZER und CHAU VU — Heinrich-Heine-Universität Düsseldorf, Universitätsstrasse 26.43.02, 40225 Düsseldorf

The large variety of possible conformers even of small biomolecular building blocks can easily be mapped to the experimentally determined spectra via their moments of inertia. On the other hand, rotationally resolved electronic spectra of large molecules are very congested due to their large moments of inertia. Classical techniques of line position assigned fits cannot be applied since a multitude of lines is overlapping within their line widths. In these cases, where classical techniques break down, the automated fitting based on genetic algorithms (GA) is very advantageous. Beyond the possibility of structure determinations in different electronic states, the line intensities and line shapes in the spectra can be used to obtain information about the excited state life time and about the electronic nature of the excited state via the transition dipole moment orientation. The applicability of the method will be shown exemplarily for the tryptamine system and the N-acetyltryptophaneylester (NATE). In the case of tryptamine the energetic ordering of the excited states is examined for various conformers. NATE is an example of a protected amino acids, that opens the way to the high resolution spectroscopy of small peptides. The stationary points on the conformational landscape of NATE will be explored using the combination of rotationally resolved LIF spectroscopy and the GA based fitting strategy.

MO 43.2 Mi 14:15 H10

**Photofragment spectroscopy of small protonated Biomolecules** — ●DIRK NOLTING — Max-Born-Institut für Nichtlineare Optik und Kurzzeitspektroskopie, Max-Born-Str. 2a, 12489 Berlin

A combination of an electrospray ion source and a Paul trap was used to investigate the spectroscopic properties of protonated model chromophores like adenine and tryptophan in the gas phase. The energy of an UV photon is above the dissociation energy, therefore the absorption

Raum: H10

of one or several photons can lead to a statistical dissociation. This can be used to probe the absorption spectra of protonated molecules. The experiments indicate that some of the relaxation pathways known from their neutral counterparts are also present in the ionic species but there are also new relaxation and dissociation pathways unique to protonated species.

MO 43.3 Mi 14:30 H10

**Nachweis starker excitonischer Pigment-Pigment-Kopplung in photosynthetischen Antennenkomplexen mittels Nichtlinearer Polarisationspektroskopie in der Frequenzdomäne** — ●BERND VOIGT<sup>1</sup>, MARIA KRUKUNOVA<sup>2</sup>, DIETER LEUPOLD<sup>1</sup>, HEIKO LOKSTEIN<sup>1</sup> und RALF MENZEL<sup>1</sup> — <sup>1</sup>Universität Potsdam, Am Neuen Palais 10, 14469 Potsdam — <sup>2</sup>Universität Hamburg, Luruper Chaussee 149, 22761 Hamburg

Die spektroskopischen Charakteristika der Subbanden in Absorptionsprofilen lichtsammlender photosynthetischer Komplexe werden sowohl durch Pigment-Pigment- als auch Pigment-Protein-Wechselwirkungen bestimmt. Strukturbedingt kann der Energietransfer (EET) zwischen den Pigmenten Förster- oder excitonischen Charakter haben und ist durch Pump-Probe-Messungen in der Zeitdomäne nur schwer aufzuklären. Nichtlineare Polarisationspektroskopie in der Frequenzdomäne (NLPF) bietet die Möglichkeit, die Art der Wechselwirkung direkt zu unterscheiden. Für den Lichtsammelkomplex LHC II konnte in Verbindung mit site-directed mutagenesis-Studien ein stark excitonisch gekoppeltes Chlorophyll (Chl) a-Homo-Dimer mit Beteiligung benachbarten Chls b nachgewiesen werden. Neueste hochaufgelöste (2.72 bzw. 2.5 Å) LHC II-Strukturmodelle bestätigten diese Befunde. Der ähnliche Komplex CP29 zeigt ebenfalls starke excitonische Chl a/Chl b-Wechselwirkungen. Für das Peridinin-Chl a-Protein (PCP) wurden starke excitonische Carotenoid/Carotenoid-Wechselwirkungen in S2 gezeigt. Dieser Beitrag wurde von der DFG im Rahmen des SFB 429 gefördert.

MO 43.4 Mi 14:45 H10

**Inelastic electron interaction (ionization/attachment) of biomolecules embedded in superfluid He droplets** — ●STEPHAN DENIFL<sup>1</sup>, FABIO ZAPPA<sup>1,2</sup>, INGO MÄHR<sup>1</sup>, PAUL SCHEIER<sup>1</sup>, and TILMANN D. MÄRK<sup>1</sup> — <sup>1</sup>Institut für Ionenphysik, Leopold-Franzens Universität Innsbruck, Technikerstr. 25, A-6020 Innsbruck, Austria — <sup>2</sup>UNESA, Rio de Janeiro, Brasil

Since the pioneering experiments by Sanche and coworkers [1] demonstrating that low energy electrons can damage plasmid DNA we have also started a series of measurements concerning inelastic electron interaction (ionization/attachment) with compounds of the DNA. First measurements were carried out with isolated biomolecules in the gas phase [2]. We extend now these measurements by embedding the biomolecules in helium droplets which leads to the formation of bio-molecular clusters. We study the behavior of these clusters upon ionization and electron attachment using a double focusing mass spectrometer and compare the results with those from isolated gas phase molecules.

This work was supported by FWF (Wien), the EU commission (Brussels, through the EPIC network and the COST Action P9). F.Z gratefully acknowledges a post-doc grant from Brazilian agency CNPq.

[1] B. Boudaiffa, P. Cloutier, D. Hunting, M. A. Huels and L. Sanche, *Science* 287 (2000) 1658

[2] S. Denifl, S.Ptasinska, M. Probst, J. Hrusak, P. Scheier and T.D. Märk, *J. Phys. Chem. A* 108 (2004) 6562-6569

MO 43.5 Mi 15:00 H10

**Ultra-sensitive Schwingungsspektroskopie sub-mikroskopischer Biomolekularer Systeme mittels CARS-Mikroskopie** — ●STEPHAN BUSCH, ALEXANDER KOVALEV, ADAM MUSCHIELOK, NANDAKUMAR PATINCHARATH und ANDREAS VOLKMER — 3. Physikalisches Institut, Universität Stuttgart, Pfaffenwaldring 57, 70550 Stuttgart, Deutschland

Die CARS-Mikroskopie ermöglicht die chemisch selektive Bildgebung auf der Grundlage des nichtlinearen optischen Phänomens der kohärenten anti-Stokes-Ramanstreuung (CARS: Coherent Anti-Stokes Raman Scattering), ohne dass die Probe mit Farbstoffen angefärbt werden müsste. Die intrinsischen molekularen Schwingungseigenschaften der Probe werden hierbei für die Kontrasterzeugung in einem optischen Mikroskop genutzt. Darüberhinaus ermöglicht die CARS Mikroskopie die ortsauflösende Schwingungsspektroskopie in der Frequenz- sowie in der Zeitdomäne. Unter Ausnutzung der intrinsischen optisch-heterodyn Detektion (OHD) des CARS Spektrums ist eine Verstärkung des Raman-resonanten Signals möglich. Dies erlaubt eine signifikant erhöhte Detektionssensitivität für die nichtinvasive und quantitative Spektroskopie. Dabei ist das gemessene CARS Signal die Interferenz des schwachen Raman-resonanten CARS Feldes des sub-mikroskopischen Objektes mit dem sehr viel intensiveren nicht-resonanten CARS der umgebenden Materie (z.B. Wasser). Letzteres agiert als lokales Oszillatorfeld in diesem OHD-CARS Detektionsverfahren. Eine Übersicht zu Anwendungen in der Biophysik wird gegeben.

MO 43.6 Mi 15:15 H10

**Systematischer Vergleich zwischen THz-TDS- und FT-IR Spektroskopie** — ●MARTIN RUMOLD, MATTHIAS HOFFMANN und HANSPETER HELM — Institut für Physik, Albert-Ludwigs-Universität Freiburg, Stefan-Meier-Straße 19, 79104 Freiburg

In den letzten 15 Jahren hat sich die THz-Time-Domain-Spektroskopie als eigenständige spektroskopische Technik weit verbreitet. Mithilfe ultrakurzer Laserpulse können Absorptionsspektren im Bereich von 5 bis 120 cm<sup>-1</sup> erhalten werden. Ein herkömmliches Fourier-Transform IR-Spektrometer mit einem heliumgekühltem Bolometer als Detektor ist ebenfalls in der Lage bis herab zu 30 cm<sup>-1</sup> Daten zu liefern. Wir untersuchen die Leistungsfähigkeit beider Gerätetypen im genannten Wellenlängenbereich und erörtern ihre jeweiligen Vor- und Nachteile im Bezug auf Probenpräparation, Meßgeschwindigkeit, Vorbereitungszeit und Systemkosten. Zur Charakterisierung verwenden wir sowohl Biomoleküle als auch anorganische Substanzen aus der Festkörperchemie.

MO 43.7 Mi 15:30 H10

**Photodissoziation von Thymin** — ●MICHAEL SCHNEIDER<sup>1</sup>, RAMAN MAKSIMENKA<sup>1</sup>, THEOFANIS KITSOPOULOS<sup>2</sup> und INGO FISCHER<sup>1</sup> — <sup>1</sup>Institut für Physikalische Chemie, Universität Würzburg, Am Hubland, D-97074 Würzburg — <sup>2</sup>Institute of Electronic Structure and Laser (IESL), Foundation for Research and Technology Hellas (FORTH), P.O. Box 1527, GR-71110 Heraklion, Greece

Wir diskutieren die Photochemie und Photodissoziationsdynamik des Thymins, die durch Zweifarben-Photofragment-Dopplerspektroskopie und Einfarben-Slice-Imaging untersucht wurden. Thymin wird optisch in einen  $\pi - \pi^*$ -Zustand angeregt, von dem bekannt ist, dass eine schnelle Deaktivierung erfolgt. Die H-Atom-Photofragmentspektren werden dominiert durch Zweiphotonenprozesse mit anschließendem statistischen Zerfall. Dies kann durch die Absorption eines zweiten Photons erklärt werden, welches das Molekül von einem langlebigen dunklen Zustand in einen hochangeregten Zustand überführt. Von diesem findet eine schnelle Deaktivierung in den Grundzustand statt. Es wurden keine Hinweise auf eine wichtige Rolle des angeregten  $\pi - \sigma^*$ -Zustands gefunden, wie er in Adenin und anderen heterocyclischen Molekülen identifiziert wurde.

MO 43.8 Mi 15:45 H10

**Tautomers and electronic states of jet-cooled 2-aminopurine investigated by double resonance spectroscopy and theory** — ●KAI SEEFELD<sup>1</sup>, CHRISTIAN PLÜTZER<sup>1</sup>, DENNIS LÖWENICH<sup>1</sup>, THOMAS HÄBER<sup>1</sup>, ROLF LINDER<sup>1</sup>, KARL KLEINERMANN<sup>1</sup>, JÖRG TATCHEN<sup>2</sup> und CHRISTEL MARIAN<sup>2</sup> — <sup>1</sup>Institut für Physikalische Chemie I, Heinrich Heine Universität Düsseldorf, Universitätsstrasse 1, 40225 Düsseldorf — <sup>2</sup>Institut für Theoretische Chemie und Computerchemie, Heinrich Heine Universität Düsseldorf, Universitätsstrasse 1, 40225 Düsseldorf

We present resonant two-photon ionization (R2PI), IR-UV, and UV-UV double resonance spectra of jet-cooled 2-aminopurine (2AP) as well as Fourier Transform InfraRed (FTIR) gas phase spectra. 2AP is a fluorescing isomer of the nucleobase adenine. The results show that there is only one tautomer of 2AP which absorbs in the wavelength range 32300-34500 cm<sup>-1</sup>. The comparison with the calculated IR spectra of 9H- and 7H-2AP points to 9H-2AP as the dominating tautomer in the gas phase but are too similar to allow an unambiguous assignment of the experimental spectra to the respective tautomer.

Hence, we determined vertical and adiabatic excitation energies of both tautomers employing combined density functional theory and multi-reference configuration interaction techniques.

## MO 44 Quantum Chemistry and Molecular Dynamics

Zeit: Mittwoch 16:30-18:15

Raum: H12

MO 44.1 Mi 16:30 H12

**2-spinor Minimax Dirac-Fock-Slater FEM Calculations for heavy two Atomic Molecules** — ●OSSAMA KULLIE und DIETMAR KOLB — Department of Natural Science, University of Kassel, Germany

2-spinor fully relativistic calculations based on the minimax principle can be done[1,2]. In this talk we discuss finite element (FEM) 2-spinor minimax Dirac-Fock-Slater calculations for strongly relativistic molecules, i. e. with heavy atoms. As examples we give, ZnO, CdO, HgO, Cu<sub>2</sub>, Ag<sub>2</sub>, Au<sub>2</sub> and UubO, UuuX, where Uuu has the charge Z=111. X stands for some atom like Au, Uuu. A comparison with traditional 4-spinor LCAO results will be given. [1] O. Kullie, D. Kolb, A. Rutkowski, *Chem. Phys. Lett.* 383, 215 (2004). [2] O. Kullie, Inaugural-Dissertation, University of Kassel (2004).

MO 44.2 Mi 16:45 H12

**Comparison of 4- and 2-spinor LCAO in Many-Electron Relativistic two-atomic Calculations** — ●HUI ZHANG und DIETMAR KOLB — FB 18, Kassel University

We have compared linear approximations to relativistic minimax (LARM) with traditional 4-spinor and kinetic balance LCAO in one electron super-heavy quasi-molecular system in a recent paper [1]. The good agreement of LARM with minimax encouraged us to apply it to many-electron molecular systems with large nuclear charge Z. Here we compare the results of both the traditional 4-spinor and LARM LCAO in order to investigate the influence of artifacts in chemical calculations, where the many-electron effects are approximated by the Dirac-Fock-Slater density functional.

[1] H. Zhang, H J Luo, J Kolb, O Kullie, and D. Kolb, *J. Phys. B: At.*

Mol. Opt. Phys. 38, 2955 (2005)

MO 44.3 Mi 17:00 H12

**Rydberg-Zustände mit der Quanten-Monte-Carlo-Methode** — ●ANNIKA BANDE und ARNE LÜCHOW — Institut für Physikalische Chemie, RWTH Aachen, Landoltweg 2, 52056 Aachen

Zum ersten Mal wurden mit der Quanten-Monte-Carlo-Methode (QMC) erfolgreich Rechnungen an Rydberg-Zuständen durchgeführt. Dazu wurden Anregungsenergien und Singulett-Triplett-Aufspaltungen in den Systemen Kohlenstoff und Kohlenmonoxid berechnet. Die betrachteten Atomzustände waren der  $^3\text{P}$ -Grundzustand sowie die  $^3\text{P}$ - und  $^1\text{P}$ -Zustände mit der Elektronenkonfiguration  $2\text{pns}$  ( $n=3-6$ ); im Molekül waren es der Grundzustand ( $^1\Sigma$ ) und die beiden darüberliegenden  $^1\Sigma$ - und  $^3\Sigma$ -Zustände. Als Guide-Wellenfunktion dienen Slater Determinanten, die aus Kohn-Sham open shell localized Hartree-Fock- (OSLHF-) Orbitalen konstruiert sind. Die Fixknoten-Diffusions-Quanten-Monte-Carlo-Methode (FN-DMC) liefert genaue Anregungsenergien, wohingegen die experimentellen Singulett-Triplett-Aufspaltungen mit dem Variations-Quanten-Monte-Carlo-Verfahren exakt wiedergegeben werden.

Da die FN-DMC-Energie stark von der Qualität der Knotenstruktur der Guide-Funktion abhängt, wurden beispielhaft die vorhandenen, durch die Knoten eingegrenzten Gebiete, analysiert. So konnten in den einzelnen Zuständen verschiedene Knotengebiete charakterisiert werden, die jeweils in unterschiedlichen Energieeigenwerten resultieren.

MO 44.4 Mi 17:15 H12

**Rotationseffekte in zeitunabhängigen quantenmechanischen Streurechnungen an mehratomigen chemischen Elementarreaktionen** — ●CARSTEN HENNIG und STEFAN SCHMATZ — Institut für Physikalische Chemie der Georg-August-Universität Göttingen, Tammannstraße 6, D-37077 Göttingen

Quantenmechanische zustandsaufgelöste Streurechnungen an chemischen Reaktionen mit sechs beteiligten Atomen sind ein aktuelles Forschungsgebiet der Theoretischen Reaktionsdynamik und stellen hohe Anforderungen an die Qualität der eingesetzten Methoden. Insbesondere stellt sich dabei das Problem der effizienten Behandlung der Drehimpulskoordinaten, für das eine kanonische Lösung nicht in Sicht ist. Im Rahmen von zeitunabhängigen quantenmechanischen Verfahren werden Methoden zur Basisadaptierung, Behandlung der Eckart-Singularitäten und generischen Trennung der Reaktionskanäle bei asymptotischen Konfigurationen vorgestellt.

Ein interessantes Anwendungsfeld sind bimolekulare nukleophile Substitutions ( $\text{S}_{\text{N}}2$ )-Reaktionen wie etwa die Chlor-Brom-Austauschreaktion  $\text{Cl}^- + \text{CH}_3\text{Br} \rightarrow \text{ClCH}_3 + \text{Br}^-$ . Aus dimensionsreduzierten Modellen lassen sich Aussagen über die reaktionsrelevanten Moden gewinnen. Rotations- und Knickschwingungseinflüssen kommt dabei auf quantenmechanischem Niveau eine große Bedeutung zu.

MO 44.5 Mi 17:30 H12

**Elektron-Kern-Korrelationen in der quanten-klassischen Beschreibung von laserinduzierter Dissoziation und Ionisation** — ●FRANK GROSSMANN, MATHIAS UHLMANN, THOMAS KUNERT und RÜDIGER SCHMIDT — ITP, TU Dresden, D-01062 Dresden

Die Untersuchung von lasergetriebenen Phänomenen im Rahmen einer gemischt quanten-klassischen Beschreibung von Molekülen ist ein hochaktuelles Forschungsgebiet. In sogenannten mean-field Zugängen zur Molekulardynamik kann die fehlende Korrelation zwischen Elektronen und Kernen jedoch zu einer ungenauen Beschreibung der Dynamik führen. Dies gilt insbesondere bei Anregung des Ionisationskontinuums.

In diesem Beitrag präsentieren wir eine näherungsweise Behandlung der Korrelation, die analog zum Tullyschen surface hopping ist. Die Anwendung der Methode wird anhand von Rechnungen für das  $\text{H}_2^+$  Molekülion in einem intensiven Laserfeld demonstriert und Unterschiede zum klassischen surface hopping werden aufgezeigt.

MO 44.6 Mi 17:45 H12

**Non-perturbative treatment of ionisation of molecular hydrogen in intense ultra-short laser pulses** — ●ALEJANDRO SAENZ and MANOHAR AWASTHI — AG Moderne Optik, Institut für Physik, Humboldt-Universität zu Berlin, Hausvogteiplatz 5-7, 10117 Berlin

Results are presented that were obtained with a recently developed numerical approach to the solution of the time-dependent Schrödinger equation (TDSE) describing the fully correlated, three-dimensional motion of the electrons of  $\text{H}_2$  in intense ultra-short laser pulses. First, a comparison of the results with the predictions from simplified models (perturbation theory, Ammosov-Delone-Krainov tunneling model, and strong-field approximation SFA) is given. The second part discusses the influence of vibrational motion on the total ionisation yield, but especially on the vibrational distribution of the formed  $\text{H}_2^+$  ions. The recent experimental results that showed a strong non-Franck-Condon distribution (in conflict with previous assumptions) were originally explained by one of us on the basis of the quasi-static approximation [1]. Since the latter is not necessarily valid an investigation using the solution of the TDSE was now performed. This is especially important in view of an alternative physical explanation based on the SFA that was very recently given for the experimentally found vibrational distribution [2].

[1] X. Urbain *et al.*, *Phys. Rev. Lett.* **92**, 163004 (2004).[2] T. K. Kjeldsen and L. B. Madsen, *Phys. Rev. Lett.* **95**, 073004 (2005).

MO 44.7 Mi 18:00 H12

**Dynamik organischer Moleküle und Fullerene in intensiven Laserfeldern** — ●JAN HANDT<sup>1</sup>, THOMAS KUNERT<sup>2</sup> und RÜDIGER SCHMIDT<sup>2</sup> — <sup>1</sup>Max-Planck-Institut für Physik komplexer Systeme, Nöthnitzer Strasse 38, D-01187 Dresden — <sup>2</sup>Institut für Theoretische Physik, Technische Universität Dresden, D-01062 Dresden

Die Dynamik organischer Moleküle und Fullerene in intensiven Laserfeldern wird voll mikroskopisch unter Berücksichtigung aller Freiheitsgrade und expliziter Behandlung des Laserfeldes untersucht. Dabei wird die sogenannte nichtadiabatische Quantenmolekulardynamik (NA-QMD) benutzt, die die Elektronen in zeitabhängiger Dichtefunktionaltheorie in Basisentwicklung und die Kerne klassisch beschreibt. Die Dynamik der beiden Systeme ist dabei selbstkonsistent miteinander gekoppelt. Insbesondere wird gezeigt, dass die Dynamik organischer Moleküle (Ethylen, Diimin) vor allem durch die geeignete Wahl der Laserfrequenz kontrolliert werden kann. Außerdem wird eine Studie zu den Eigenschaften der Atmungsmode von  $\text{C}_{60}$  bei hohen Anregungsenergien vorgestellt.

## MO 45 Biomolecules II

Zeit: Mittwoch 16:30–18:30

Raum: H10

MO 45.1 Mi 16:30 H10

**Femtosecond Two-Photon Spectroscopy determines hidden carotenoid dark state dynamics** — ●PETER JOMO WALLA<sup>1,2</sup>, WEHLING AXEL<sup>2</sup>, and MICHAEL HILBERT<sup>1</sup> — <sup>1</sup>Max-Planck-Institut für Biophysikalische Chemie, Am Faßberg 11, D-37077 Göttingen — <sup>2</sup>Institut für Physikalische und Theoretische Chemie, Abt. Biophysikalische Chemie, Hans-Sommerstr. 10, D-38106 Braunschweig

Carotenoids play an important role as light-harvesting pigments and in the regulation of the energy flows in the photosynthetic apparatus under changing environmental light conditions. However, a detailed insight in the underlying mechanisms was very often impossible due the optical forbidden character of the first excited state of carotenoids, Car S1. This is because it has the same Ag symmetry as the ground state, Car S0. An elegant approach is the investigation via two-photon excitation because Ag->Ag-transitions are generally two-photon allowed. Using this

approach we access directly and selectively the forbidden state and gain important information about the light harvesting mechanisms and the regulation of excessive excitation energy under high-light conditions in the photosynthetic apparatus. We will present latest femtosecond two-photon results from several photosynthetic protein complexes and real plants. With these data it is possible to gain a detailed understanding of the energy transfer mechanisms and the regulation of the photosynthetic apparatus in living plants.

MO 45.2 Mi 16:45 H10

**Spektroskopie optisch dunkler Carotenoid-Anregungszustände mittels simultaner Zweiphotonen-Fluoreszenz-Anregung durch fs-Laserpulse** — ●ALEXANDER BETKE<sup>1</sup>, BERND VOIGT<sup>1</sup>, MARIA KRIVONOVA<sup>2</sup>, DIETER LEUPOLD<sup>1</sup>, HEIKO LOKSTEIN<sup>1</sup> und RALF MENZEL<sup>1</sup> — <sup>1</sup>Universität Potsdam, Am Neuen Palais 10, 14469 Potsdam — <sup>2</sup>Universität Hamburg, Luruper Chaussee 149, 22761 Hamburg

Carotenoide haben in photosynthetisierenden Organismen wichtige Funktionen: als Strukturkomponenten der Pigment-Protein-Komplexe, als accessorische lichtsammelnde Pigmente, und in der Photoprotektion. An den beiden letztgenannten Funktionen sind optisch "dunkel", d.h. durch Einphotonenabsorption nicht zugängliche Zustände beteiligt, die in enger energetischer Nachbarschaft von (Bacterio-)Chlorophyll-Anregungszuständen liegen. Ein methodischer Ansatz, die Rolle der "dunklen" Zustände beim Anregungsenergie-Transfer und der Dissipation überschüssiger Anregungsenergie in Lichtsammel-Komplexen (LH-Cs) zu studieren, ist die mittels (Bacterio-)Chlorophyllfluoreszenz detektierte simultane Zweiphotonenabsorption von durchstimmbaren fs-NIR-Impulsen. Im Vortrag werden Vor- und Nachteile dieses Ansatzes und experimentelle Details vorgestellt, sowie neuere Ergebnisse diskutiert. Dieser Beitrag wird von der DFG im Rahmen des SFB 429 gefördert.

MO 45.3 Mi 17:00 H10

**Energy flow in  $\beta$ -carotene after multiphoton excitation using tunable sub-30 fs pulses in the near-IR** — ●TIAGO BUCKUP, ALEXANDER WEIGEL, and MARCUS MOTZKUS — Physikalische Chemie, Phillips Universität Marburg, 35043 Marburg, Germany

Carotenoids perform a variety of critical functions in nature, which are strongly dependent on their energy deactivation network. The classical three-level-scheme of carotenoids describes the deactivation of the photoexcited  $S_2$  state by ultrafast internal conversion to the dark  $S_1$  state which in turn decays to the ground state  $S_0$  on the picosecond time scale. As it has been shown in previous contributions, the  $S_1$  state can be excited via a two-photon transition directly from  $S_0$ . Here we extend the concept of multiphoton Pump-Probe spectroscopy to beta-carotene in a new excitation range (900-1100 nm) using tunable sub-30 fs pulses. Besides the well-known  $S_1$  deactivation, long-lived contributions can also be observed in the blue region of the visible spectra and in the near-IR. These two contributions are associated with the absorption of a triplet and a cation state, respectively. The presence of additional dark states is also considered and a model taking into account all observations is presented.

MO 45.4 Mi 17:15 H10

**Thymine dimer formation probed by femtosecond infrared spectroscopy** — ●WOLFGANG SCHREIER<sup>1</sup>, TOBIAS SCHRADER<sup>1</sup>, FLORIAN KOLLER<sup>1</sup>, PETER GILCH<sup>1</sup>, WOLFGANG ZINTH<sup>1</sup>, and BERN KOHLER<sup>2</sup> — <sup>1</sup>Ludwig-Maximilians-Universität, Department of Physics, Chair for BioMolecular Optics, Oettingenstr. 67, 80538 München — <sup>2</sup>The Ohio State University, Department of Chemistry, 100 West 18th Avenue, Columbus, Ohio 43210

Absorption of UV radiation by DNA bases is known to induce harmful mutagenic products. One major photoproduct at bipyrimidine sites is the photodimerization of neighboring thymine residues. Despite the intense work in this field there is still a lack of information regarding the time scale at which these dimers are formed [1], [2].

We used time resolved UV pump, IR probe spectroscopy to investigate the 18-mer of single-stranded thymidylic acid [(dT)<sub>18</sub>] and the corresponding mononucleotide (thymidine monophosphate, TMP). We show that femtosecond infrared spectroscopy can address dimer specific marker bands between 1300 and 1500  $\text{cm}^{-1}$  and that the excitation of the oligonucleotide leads to the formation of cyclobutane dimers in less than 20 ps. Additionally we find no slow growth in these marker bands as expected for a triplet intermediate. This points to a singlet precursor for these photoproducts.

[1] Crespo-Hernandez CE, Cohen B, Kohler B, NATURE 436 (7054): 1141-1144 (2005)

[2] Marguet S, Markovitsi D, JACS 127 (16): 5780-5781 (2005)

MO 45.5 Mi 17:30 H10

**Photoinduced conformational dynamics of a photoswitchable peptide: A nonequilibrium molecular dynamics simulation study** — ●PHUONG HOANG NGUYEN, ROMAN GORBUNOV, and GERHARD STOCK — Institute of Physical and Theoretical Chemistry, J. W. Goethe University, Marie-Curie-Str. 11, D-60439 Frankfurt, Germany

Recent advances in femtosecond laser experiments allow for real-time observations and true-multidimensional views of the dynamics of chemical reactions. A beautiful example is the femtosecond infrared spectroscopy experiments on photoswitchable peptides which provide a new and promising way to study the peptide folding and unfolding in unprecedented detail[1,2]. To obtain an appropriate theoretical description of these experiments, we suggest to extend well-established all-atom molecular dynamics simulation techniques to the description of nonequilibrium photoinduced conformational dynamics in peptides[3]. We then performed the true nonequilibrium molecular dynamics simulations on the octapeptide which is covalently bound to both ends of an azobenzene conformational switch. This study allows us to monitor the progress of photoinduced peptide folding, including cooling phase, global and local conformational rearrangements, and photoinduced spectral response. The results are discussed in the light of experiments[1,2].

References

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[2] J. Bredenbeck et al., J. Phys. Chem. B 107, 8654 (2003).

[3] P. H. Nguyen and G. Stock, Chem. Phys. (in press).

MO 45.6 Mi 17:45 H10

**First Steps of Retinal Photoisomerization in Protorhodopsin** — ●MARTIN O. LENZ<sup>1</sup>, ROBERT HUBER<sup>1</sup>, BERNHARD SCHMIDT<sup>2</sup>, PETER GILCH<sup>2</sup>, ROLF KALMBACH<sup>3</sup>, MARTIN ENGELHARD<sup>3</sup>, and JOSEF WACHTVEITL<sup>1</sup> — <sup>1</sup>Institut für Physikalische und Theoretische Chemie, Marie-Curie-Str. 11, Johann-Wolfgang-Goethe-Universität Frankfurt, 60439 Frankfurt am Main — <sup>2</sup>Universität München, Department für Physik, Lehrstuhl für BioMolekulare Optik, Oettingenstraße 67, 80538 München — <sup>3</sup>Max-Planck-Institute of Molecular Physiology, Department of Physical Biochemistry, Otto-Hahn-Str. 11, 44227 Dortmund

The early steps ( $< 1$  ns) in the photocycle of the proton pump protorhodopsin (PR) are analyzed by ultrafast spectroscopic techniques. A comparison to the first primary events of well known retinal proteins like the archaeal proton pump bacteriorhodopsin (BR) is given. A dynamic Stokes shift observed in fs-time resolved fluorescence experiments allows a direct observation of early motions on the excited state potential energy surface. The initial dynamics is dominated by sequentially emerging stretching ( $< 150$  fs) and torsional ( $\sim 300$  fs) modes of the retinal. The different protonation states of the primary proton acceptor Asp97 drastically affect the reaction rate and the overall quantum efficiencies of the isomerization reactions mainly evidenced for time scales above 1 ps. However, no major influence on the fast time scales could be seen, indicating that the movement out of the Franck-Condon region is fairly robust to electrostatic changes in the retinal binding pocket. Taking into account investigations on the primary events of BR a reaction scheme is presented.

MO 45.7 Mi 18:00 H10

**Primäre Dynamik der Mutante D85T des Transmembranproteins Bakteriorhodopsin** — ●CONSTANZE SOBOTTA<sup>1</sup>, MARKUS BRAUN<sup>1</sup>, JÖRG TITTOR<sup>2</sup> und WOLFGANG ZINTH<sup>1</sup> — <sup>1</sup>Lehrstuhl für BioMolekulare Optik, Oettingenstr. 67, Ludwig-Maximilians-Universität München, 80538 München — <sup>2</sup>Max-Planck-Institut für Biochemie, Am Klopferspitz 18, 82152 Martinsried

Das Archaeon Halobacterium salinarum lebt unter nativen Bedingungen in Umgebungen mit sehr hohen Salzkonzentrationen. In der Membran des Bakteriums befinden sich die Transmembranproteine Bakteriorhodopsin (BR) und Halorhodopsin (HR). Obwohl die Proteine strukturell sehr ähnlich sind, unterscheiden sie sich zum einen in ihrer Primärreaktion und zum anderen auch in ihrer Funktion als lichtgetriebene Protonen- bzw. Chlorid-Pumpe. Als wichtigster Unterschied der BR- und HR-Struktur wurde die Ladung der Aminosäure an der Position 85 (BR: Aspartat; HR: Threonin) in der Nähe der Schiffchen Base (Retinal-Chromophor) identifiziert, welche das optische Spektrum und die Dynamik der Isomerisierungsreaktion des Retinal-Chromophors verändert.

Daher wurden femtosekunden-zeitaufgelöste transiente Absorptionmessungen an punktmutierten BR-Proteinen D85T (Aspartat wird er-



setzt durch Threonin) durchgeführt. Durch Änderung von pH-Wert und Salzkonzentration soll so die Ladung an der Stelle 85 gezielt variiert werden. Es zeigt sich, dass die Isomerisierung beeinflusst wird und je nach Wahl der eingestellten Bedingungen eher der Dynamik von BR bzw. HR ähnelt.

MO 45.8 Mi 18:15 H10

**Photoinduced processes in microhydrated adenine clusters** — ●ELENA SAMOYLOVA, V. R. SMITH, T. SCHULTZ, H.-H. RITZE, W. RADLOFF, and I.V. HERTEL — Max-Born-Institut Berlin, Max-Born Strasse 2a, 12489 Berlin, Germany

Photochemical reactions can be efficiently quenched by fast radiationless decay to the electronic ground state. We investigate such mechanisms in DNA, first, in isolated bases followed by bigger and microhydrated clusters using time-resolved ion and electron spectroscopy. For adenine-monomer the excited state dynamics could be characterized by an expo-

ponential decay containing two components with 100 fs and 1 ps life time. The 100 fs component is due to a very short living electronic state of  $\pi\pi^*$  character and the 1 ps component is due to an optically dark  $n\pi^*$  state. In the microhydrated adenine we did not observe the 1 ps contribution. That indicated a different very fast relaxation pathway due to a  $\pi\sigma^*$  electronic state. In adenine-dimer we found a similar mechanism of excited state deactivation as for A(H<sub>2</sub>O), with a minor contribution of the  $n\pi^*$  state. Very different behaviour was observed in adenine-dimer cluster with three or more water molecules when the cluster changed from a planar, H-bound to a  $\pi$ -stacked structure. With photoelectron-photoion coincidence spectroscopy an additional relaxation pathway with ns life time was identified which we assigned to the formation of an eximer state. Our observations in the gas phase reproduce similar experiments in water solution and are discussed in the context of high-level theoretical calculation.

## MO 51 Molecular Quantum Control

Zeit: Donnerstag 10:40–12:40

Raum: H12

MO 51.1 Do 10:40 H12

**Population transfer in the multi-photon excitation of molecules** — ●VOLKER ENGEL, MARCO ERDMANN, and STEFANIE GRÄFE — Institut für Physikalische Chemie, Universität Würzburg, Am Hubland, \*D-97074 Würzburg, Germany

The laser induced selective preparation of electronically excited molecular states is investigated, where the instantaneous dynamical response of the system to an applied field is employed to determine the latter. By construction, the obtained pulses carry the signature of the electronic and nuclear motion [1]. It is shown that an effective population transfer to different target states is possible. Time-dependent photoelectron spectra are calculated to illustrate that the achieved control yields can be measured directly [2].

[1] S. Gräfe, C. Meier, and V. Engel, *J. Chem. Phys.* **122**, 184103 (2005).

[2] S. Gräfe, M. Erdmann, and V. Engel, *Phys. Rev. A* **72**, 013404 (2005).

MO 51.2 Do 10:55 H12

**Pulse shaping control of spatially aligned rotational wavepackets of N<sub>2</sub> and O<sub>2</sub>** — ●CHRISTIAN HORN<sup>1</sup>, MARC KRUG<sup>1</sup>, MATTHIAS WOLLENHAUPT<sup>1</sup>, THOMAS BAUMERT<sup>1</sup>, REBECA DE NALDA<sup>2</sup>, FLORIAN AUSFELDER<sup>2</sup>, and LUIS BANARES<sup>2</sup> — <sup>1</sup>Universität Kassel, Institut für Physik und Center for Interdisciplinary Nanostructure Science and Technology (CINSaT), Heinrich-Plett-Str. 40, D-34132 Kassel, Germany — <sup>2</sup>Dpto. Química Física I, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, Avda. Complutense s/n, 28040 Madrid, Spain

Molecular alignment induced by ultrashort laser pulses has proven to be a powerful tool to create spatially aligned distributions in an otherwise randomly oriented, gaseous sample of molecules. The field-free alignment occurring at revivals of the rotational wave-packet is characterized by very fast dynamics where diatomic molecules oscillate between the situation of alignment (molecular axis preferentially oriented along the direction of the laser polarization vector) and anti-alignment, where the molecular axis preferentially lies in the plane perpendicular to the polarization vector. Previous theoretical and experimental work has been devoted to affect the magnitude and intensity of such revivals by using either pairs, or sequences of pulses. A much more general approach to control is the use of pulse-shaping techniques. We show that phase-only shaping of pulses can be successfully applied to the control of alignment revivals. Specifically we are able to enhance alignment at the expense of anti-alignment or vice versa at a given revival by applying a suitable phase mask to the aligning laser pulse. The results of the experiment are compared with numerical simulations.

MO 51.3 Do 11:10 H12

**Phase locked Pulse Pairs Spectroscopy on Halogens in solid Ar** — ●HEIDE IBRAHIM<sup>1</sup>, MIZUHO FUSHITANI<sup>1</sup>, MARKUS GÜHR<sup>1,2</sup>, and NIKOLAUS SCHWENTNER<sup>1</sup> — <sup>1</sup>Institut für Experimentalphysik, Freie Universität Berlin, D-14195 Berlin — <sup>2</sup>Stanford Synchrotron Radiation Laboratory, Menlo Park, California 94025-7015

We used an unbalanced Michelson Interferometer to obtain phase locked pulse pairs (PLPP) for spectroscopy on halogens in rare gas matrices. The chirp difference between the two arms was optimized to match the electronic B state anharmonicity of the molecule. The decaying mod-

ulation contrast in the PLPP spectrum indicates a loss of electronic coherence in the range around 1 ps for Cl<sub>2</sub> [1] and Br<sub>2</sub> in an Ar matrix. From vibrational wavepacket revivals and focussing we determine the vibrational coherence time of Br<sub>2</sub> and Cl<sub>2</sub> in solid Ar to be 3 ps [1,2]. Comparison with simulations of the PLPP spectrum, taking only into account the B state absorbance, indicates a further contribution in the PLPP spectra, most likely from the lower lying A state continuum. Changing the relative phase of the two pulses allows us to prepare vibrational wavepackets predominantly composed of Zero Phonon Lines (weakly interacting with the matrix) or of Phonon Side Band (strong interaction) and thereby coherently control the molecule-lattice interaction.

[1] M.Fushitani, M.Bargheer, M.Gühr and N.Schwentner, *PCCP*, **7**, 3143 (2005)

[2] M.Gühr, H.Ibrahim and N.Schwentner, *PCCP*, **6**, 5353 (2004)

MO 51.4 Do 11:25 H12

**Enhancement of Population Transfer and Coherent Vibrations in Nile Blue (LD 690) with Phase Modulated Femtosecond Pulses** — ●JÜRGEN HAUER, TIAGO BUCKUP, and MARCUS MOTZKUS — Philipps-Universität, Physikalische Chemie, D-35032 Marburg, Germany

Coherent control of vibrational modes is essential for manipulating photochemistry on ground and excited states. We present an open loop control scheme for mode selective excitation and also for population transfer to the excited state of a dye molecule (Nile Blue). In a spatial light modulator, a sinusoidal modulation is applied in order to obtain pulse trains with well defined spacings between the sub-pulses. We show that these pulse trains allow for a more effective population transfer to the excited state than a Fourier limited pulse of equal energy. Independently thereof, the amplitude of the skeleton mode in Nile Blue at 600 cm<sup>-1</sup> is also increased by a factor of up to 1.5, depending on the pump wavelength. In order to explain the nature of the observed enhancement effect, we compare the amplification factor of pulse trains compared to unshaped pulses at different excitation wavelengths. We also perform a chirp scan on the pump pulse, indicating that either ground or excited state wavepackets are observed, depending on the pump wavelength.

MO 51.5 Do 11:40 H12

**Selective Spectral Filtering of Molecular Modes in Solution Phase Using Optimal Control in Four-Wave-Mixing Spectroscopy** — ●J. KONRADI, A.V. SCARIA, A.K. SINGH, and A. MATERNY — International University Bremen, Germany

Due to their many degrees of freedom, femtosecond time-resolved four-wave mixing (FWM) techniques like CARS (coherent anti-Stokes Raman scattering) give access to different aspects of ultrafast dynamics. While the temporal resolution is high in fs spectroscopy, the resulting signals only have a poor spectral resolution. Coherent control techniques using tailored laser pulses allow for a manipulation of molecular multi-mode dynamics. Recently, we have demonstrated, that by shaping the pulses using a learning-loop optimal control scheme, in the FWM-spectrum vibrational modes can be selectively enhanced or suppressed [1]. Here, the ratio of the signal intensities for different lines in the nonlinear Raman spectrum served as feedback signal for an evolutionary algorithm.

In our contribution we will present our latest results on frequency selective femtosecond spectroscopy. We have applied the optimal control technique in combination with electronically resonant as well as nonresonant four-wave mixing processes. We will demonstrate that in both cases the spectral resolution can be improved considerably by keeping the temporal resolution high. In order to gain information about the fundamental mechanism behind the spectrum control, an analysis of the experimental data has been performed, which will be discussed in detail.

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

MO 51.6 Do 11:55 H12

**Enhancement of Raman Modes in the Ground State of all-trans- $\beta$ -Carotene by Coherent Control** — ●J. HAUER<sup>1,2</sup>, H. SKENDEROVIC<sup>2,3</sup>, K.-L. KOMPA<sup>2</sup>, and M. MOTZKUS<sup>1,2</sup> — <sup>1</sup>Philipps-Universität, 35032 Marburg — <sup>2</sup>Max-Planck-Institut für Quantenoptik, 85748 Garching — <sup>3</sup>Institute of Physics, 10000 Zagreb

The vibrational ground state modes of  $\beta$ -carotene in solution are investigated with DFWM (degenerate four wave mixing) under resonant and non-resonant conditions in an open loop coherent control experiment with a spatial light modulator. Two of the three excitation pulses in the sequence are phase modulated by a sine function in order to obtain pulse trains with a well defined spacing between the sub pulses. Comparing the transients after resonant and the non-resonant excitation reveals that modes are not only filtered out but under resonant conditions also enhanced in their intensity compared to the Fourier-limited case. As we demonstrated in an earlier work, no such effect is observed with a non-resonant DFWM-sequence. For a better understanding of this amplification, we conduct a conventional Pump/Probe experiment in an oxazine dye (LD 690). This allows us to demonstrate that the observed effects are due to an enhanced population transfer between electronic states and an increased vibrational coherence.

MO 51.7 Do 12:10 H12

**Coherent Control with Actively Shaped Supercontinuum from a Photonic Crystal Fiber** — ●B. VON VACANO, W. WOHLLEBEN, and M. MOTZKUS — Phys. Chem., Philipps-Universität, 35032 Marburg

Coherent control aims at selectively manipulating quantum states through the interaction with laser light. To do this, broadband excitation sources are highly attractive, as ultrashort pulses offer many possible interfering quantum paths. It would be very desirable to extend the applicability of standard 100 fs - Ti:Sa-oscillators towards broadband excitation.

This can be achieved by nonlinear broadening of the laser spectrum in a microstructured fibre into supercontinuum and subsequent compression.

We successfully employed the combination of broadband pulses from a photonic crystal fibre (PCF) and pulse shaping for coherently controlled nonlinear spectroscopy [1]. The pulse shaper not only manages to compress the PCF supercontinuum to 18 fs pulses but also to additionally manipulate the phase for quantum control experiments. This approach is demonstrated by single-beam coherent anti-Stokes Raman (CARS) microspectroscopy [2,3] and is due to its simplicity well suited for general applications in coherently controlled spectroscopy and microscopy.

[1] B. von Vacano, W. Wohlleben, M. Motzkus. *Optics Letters*, in press.

[2] N. Dudovich, D. Oron, Y. Silberberg. *Journal of Chemical Physics* **118** (20), 9208 (2003).

[3] B. von Vacano, W. Wohlleben, M. Motzkus. *Journal of Raman Spectroscopy*, in press.

MO 51.8 Do 12:25 H12

**Neurale Netzwerke in der Optimalen Kontrolle** — ●REIMER SELLE, GERHARD VOGT, TOBIAS BRIXNER und GUSTAV GERBER — Physikalisches Institut, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

Evolutionäre Algorithmen haben zusammen mit der Formung ultrakurzer Laserpulse zu beachtlichen Erfolgen bei der optimalen Kontrolle chemischer Reaktionen und anderer quantenmechanischer Prozesse geführt. Unglücklicherweise lassen sich aus den optimalen Pulsformen nur sehr bedingt Rückschlüsse auf die wirksamen Kontrollmechanismen ziehen.

Nun lässt sich jedoch ein solches Optimierungsexperiment auch als eine Abbildung der vom Pulsformer generierten elektrischen Felder auf die gemessenen Observablen betrachten. Neuronale Netzwerke haben sich durch ihre hohe Genauigkeit als Werkzeug zur Approximierung solcher Abbildungen bewährt. Nach dem Durchlaufen eines Lernprozesses, während dessen Beispieldaten dieser Abbildung gelernt werden, ist das Netzwerk fähig, über diese Daten hinaus zu verallgemeinern.

Sowohl im Falle der Erzeugung der zweiten Harmonischen (SHG), als auch bei der laserinduzierten Fluoreszenz eines Laserfarbstoffs (NK88) konnte gezeigt werden, dass sich Neuronale Netzwerke zur Modellierung dieser Prozesse eignen.

Falls sich Neuronale Netzwerke auch bei der Modellierung von Prozessen bewähren, die typisch quantenmechanische Interferenzphänomene beinhalten, so könnten sie eine interessante Möglichkeit zur realistischen Modellierung von Experimenten bieten. Diese Modellierung könnte z.B. auch einen Beitrag zum Auffinden relevanter Kontrollparameter leisten.

## MO 52 Cold molecules I

Zeit: Donnerstag 10:40–12:40

Raum: H10

### Fachvortrag

MO 52.1 Do 10:40 H10

**Water vapor at one kelvin** — ●P.W.H. PINKSE<sup>1</sup>, T. RIEGER<sup>1</sup>, T. JUNGLER<sup>1</sup>, S.A. RANGWALA<sup>1</sup>, G. REMPE<sup>1</sup>, and J. BULTHUIS<sup>2</sup> — <sup>1</sup>Max-Planck-Institut für Quantenoptik, Hans-Kopfermann-Str. 1, 85748 Garching. — <sup>2</sup>Department of Physical Chemistry and Laser Centre, Vrije Universiteit, De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands

Cold dilute molecular systems are an emerging front line at the interface of quantum optics and condensed matter physics. Cold gases of dipolar molecules can be produced by forging a tight bond between two chemically distinct species of laser-cooled atoms. Alternatively, cold gas ensembles can be created by buffer gas loading or electric field manipulation of naturally occurring molecules. However, so far all the cold molecules produced in this manner have a Stark effect which is predominantly linear in the experimentally relevant electric-field range of 0-150 kV/cm.

We report the creation of a confined slow beam of heavy-water (D<sub>2</sub>O) molecules with a translational temperature around 1 kelvin. This is achieved by filtering slow D<sub>2</sub>O with inhomogeneous electrostatic fields acting on the purely quadratic Stark shift of D<sub>2</sub>O. Further, on the basis of elementary molecular properties and understanding of our filter technique [1] we predict that in the resulting slow molecular beam of D<sub>2</sub>O only a few molecular ro-vibrational states are significantly populated. [2]

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

[2] T. Rieger, et al., arXiv/physics 0512119 (2005).

MO 52.2 Do 11:10 H10

**Wege zur Manipulation der schweltnahen Photodissoziation von SO<sub>2</sub> in kaltes SO und O** — ●S. JUNG, E. TIEMANN und CH. LISDAT — Institut für Quantenoptik, Universität Hannover, Welfengarten 1, 30167 Hannover

Aus kalten SO<sub>2</sub> Molekülen können durch Anregung eines prädissoziierenden Zustandes kalte Fragmente SO und O erzeugt werden [1]. Beide Fragmente liegen im elektronische Grundzustand vor. Die Überschussenergien der bei der Dissoziation entstehenden Fragmente liegen im Bereich weniger 100 mK. Findet der Dissoziationsprozess in elektrischen Feldern statt, so verursacht der Starkeffekt eine Verschiebung der Energieniveaus der einzelnen Spezies. Durch geeignete Wahl des elektrischen Feldes können die Überschussenergien variiert und so auch zu null gebracht werden. Den Starkeffekt und damit das Dipolmoment des  $\tilde{C}^1B_2$  Zustandes haben wir experimentell ermittelt. Der Starkeffekt des SO ist bekannt und der des Sauerstoffs ist vernachlässigbar klein. Die Messergebnisse erlauben eine Vorhersage zur Variation der Überschussenergien und sollen in dem Beitrag diskutiert werden. In unserem Experiment wird ein geschwindigkeits- und rotationsgekühlter SO<sub>2</sub> Molekülstrahl durch adiabatische Expansion ins Vakuum erzeugt. Moleküle in einem schwachfeldsuchendem Zustand werden mit einer Kette von inhomogenen elektrischen Feldern abgebremst und sollen zum Stillstand gebracht werden, um sie dann in einer elektrostatischen Falle zu fangen. Die mit dieser Methode erzeugten kalten und quantenzustandsselektierten Molekülen sollen dann photodissoziiert werden.

[1] S. Becker *et al.* Chem. Phys. Lett. **208**, 15, 1993.

MO 52.3 Do 11:25 H10

**Deceleration of Benzonitrile** — ●KIRSTIN WOHLFART, FRANK FILSINGER, HENDRICK L. BETHLEM, JOCHEN KÜPPER, and GERARD MEIJER — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin

During the last years our group has been developing methods to decelerate and cool neutral, polar molecules using time varying electric fields [1]. In order to extend this technique to large or heavy molecules, which have practically only high-field seeking states, Alternate Gradient focusing must be applied. Our group showed that this technique can be used to focus and decelerate molecules in high-field seeking states [2].

We have setup a new dedicated experiment for the focusing and deceleration of large molecules using a modular design, allowing to extend the beamline as required. Using one module we have decelerated metastable CO and benzonitrile ( $C_7H_5N$ ). Benzonitrile is detected state specific using a narrow linewidth frequency doubled cw ring-dye-laser. Monitoring the integrated laser induced fluorescence after  $S_1 \leftarrow S_0$   $0_0^0$  excitation full time of flight profiles can be observed for every molecular packet passing through the laser beam. Here the results on the deceleration of benzonitrile in different rotational states are presented and future experiments for deceleration of larger molecules will be discussed.

[1] H. L. Bethlem and G. Meijer, *Int. Rev. Phys. Chem.* **22**, 73-128 (2003)

[2] H. L. Bethlem, A. J. A. van Roij, R. T. Jongma and G. Meijer, *Phys. Rev. Lett.* **88**, 133003 (2002)

MO 52.4 Do 11:40 H10

**An AC electric trap for molecules in high-field seeking states** — ●JACQUELINE VAN VELDHOVEN<sup>1</sup>, HENDRICK L. BETHLEM<sup>1,2</sup>, MELANIE SCHNELL<sup>1</sup>, and GERARD MEIJER<sup>1</sup> — <sup>1</sup>Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany — <sup>2</sup>Laser Centre Free university, Amsterdam, the Netherlands

The absolute ground state of any molecule is high-field seeking. It is therefore very important to develop deep traps with large volumes for molecules in high-field seeking states. Only ground state molecules can be evaporatively cooled, as trap loss due to inelastic collisions is avoided. Furthermore, only traps for molecules in high-field seeking states can be used to trap heavier molecules with small rotational constants.

A maximum of the static electric field in free space can be created in one or two dimensions only. In a cylindrically symmetric geometry, for instance, a static electric field can be made with a maximum in the radial and a minimum in the axial direction, or vice versa. Switching between these two saddle point configurations results in a field that is alternately focusing and defocusing in each direction for molecules in high-field seeking states. At the right switching frequency the overall effect is focusing, and confinement in three dimensions can thus be obtained.

We here report on the trapping of ammonia molecules in both high-field and low-field seeking states in such a novel AC electric trap. We have studied the stability of the AC electric trap as a function of switching frequency, and we have characterized the spatial distribution and the temperature of the trapped cloud of molecules [1].

[1] J. van Veldhoven, H.L. Bethlem and G. Meijer, *PRL* **94**, 083001 (2005).

MO 52.5 Do 11:55 H10

**Development of traps for ground-state molecules** — ●MELANIE SCHNELL, PETER LÜTZOW, JACQUELINE VAN VELDHOVEN, BRETISLAV FRIEDRICH, and GERARD MEIJER — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Abt. Molekülphysik, Faradayweg 4-6, 14195 Berlin

Cold molecules offer unique possibilities for studying cold collisions,

molecular Bose-Einstein condensates (BEC), or performing high-resolution spectroscopy experiments. For these experiments confining molecules in a trap is either necessary or will enhance the potential of the method considerably. We are developing traps for molecules in high-field seeking (hfs) states, since states of larger molecules as well as the ground state of any molecule will always be hfs. Since in such a trap it is possible to confine the molecular ground state it will also be possible to increase their phase-space density via evaporative cooling, as trap loss due to inelastic collisions can be avoided.

The generation of a static electric field maximum in free space is impossible, so that traps for molecules in hfs states have to employ time-dependency. Here we report on the development of different kinds of traps for molecules in hfs states. One kind considers switched static electric fields (ac traps) while another approach consists of a deep trap for ground-state molecules using near-resonant microwave radiation. Molecules in hfs states will be trapped in the amplitude maximum of the standing wave microwave field in an open near-confocal Fabry-Perot type resonator. Besides the characterization of the traps we will present prospects for their applications in high-resolution spectroscopic studies and for evaporative cooling experiments.

MO 52.6 Do 12:10 H10

**Sympathetic cooling of singly-protonated polyatomic molecules to sub-Kelvin temperatures** — ●ALEXANDER WILSON, CHAOBO ZHANG, DAVID OFFENBERG, ALEXANDER OSTENDORF, BERNHARD ROTH, and STEPHAN SCHILLER — Heinrich-Heine-Universität Düsseldorf

Alexa Fluor 350, a fluorescent dye molecule of mass 410 AMU, has been transferred from an electro spray ionisation (ESI) source to a linear Paul trap. Around 2300 laser-cooled  $^{138}\text{Ba}^+$  ions in a Coulomb crystal were used to sympathetically cool approximately 600 Alexa Fluor ions to below 100 mK. Observations are well described by molecular dynamic simulations, which are used to determine the number of ions, their spatial distribution and translational temperature. The ESI technique should allow many different kinds of molecules to be transferred for trapping and sympathetic cooling; of particular interest may be molecules of very high mass and those of biological relevance, indeed, Alexa Fluor 350 is usually used in biological studies for protein labelling.

MO 52.7 Do 12:25 H10

**Magnetic trapping of buffer gas loaded atoms and molecules** — ●MICHAEL STOLL<sup>1,2</sup>, JOOST M. BAKKER<sup>1,2</sup>, GERARD MEIJER<sup>1</sup>, and ACHIM PETERS<sup>2</sup> — <sup>1</sup>Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany — <sup>2</sup>Department for Quantum Optics and Metrology, Humboldt-Universität zu Berlin, Berlin, Germany

We report on the successful buffer-gas loading and trapping of atomic Chromium in a quadrupole magnet using a  $^3\text{He}$ - $^4\text{He}$  dilution refrigerator. The technique to buffer gas cool neutral molecules can provide samples of cold molecules with very high densities. Such dense samples of ultracold molecules can form a starting point for a large variety of experiments. Among these are the formation of a molecular quantum gas, ultra-high resolution spectroscopic measurements to test fundamental physics and the study of interactions between ultracold molecules. In the present experiment chromium atoms have been trapped for periods of minutes.

We observed densities exceeding  $10^{13}$  particles per  $\text{cm}^3$  and temperatures below 400mK. Trap loss is mainly due to evaporative cooling of the isolated sample. These results constitute the first successful buffer-gas loading experiment in Europe, and the extension of the technique to load and trap neutral polar molecules is readily foreseen.

## MO 53 Molecular Quantum Computing

Zeit: Donnerstag 14:00–16:00

Raum: H12

### Fachvortrag

MO 53.1 Do 14:00 H12

**Efficient implementation of three-qubit quantum gates and experimental demonstration by NMR** — ●BJÖRN HEITMANN<sup>1</sup>, NAVIN KHANEJA<sup>2</sup>, HAIDONG YUAN<sup>2</sup>, ANDREAS SPÖRL<sup>1</sup>, THOMAS SCHULTE-HERBRÜGGEN<sup>1</sup>, and STEFFEN J. GLASER<sup>1</sup> — <sup>1</sup>Department Chemie, TU München, Lichtenbergstrasse 4, 85747 Garching, Germany — <sup>2</sup>Division of Applied Sciences, Harvard University, Cambridge, MA 02138, USA

High resolution nuclear magnetic resonance (NMR) currently provides

one of the most advanced approaches for the experimental realization of quantum computing concepts. In this talk efficient ways to synthesize quantum gates in three-qubit systems by creating effective interactions between indirectly coupled spins. More specifically, we provide an efficient synthesis of a CNOT gate between two spins that are indirectly coupled via Ising-type couplings to a third spin. Our implementation of the CNOT gate is twice as fast as conventional approaches. This efficient realization of the quantum gate corresponds to computing sub-Riemannian geodesics (1,2) on the unitary group. We provide an experimental realization of the fast indirect CNOT gate on a linear three-spin chain with Ising couplings.

The new methods have important applications in quantum information processing and coherent spectroscopy.

References: (1) N. Khaneja, R. W. Brockett, S. J. Glaser, *Time Optimal Control in Spin Systems*, Phys. Rev. A 63, 03208 2001.

(2) N. Khaneja, S. J. Glaser, R. W. Brockett, *Sub-Riemannian Geometry and Time Optimal Control of Three Spin Systems: Quantum Gates and Coherence Transfer*, Phys. Rev. A, 65, 032301 2002.

MO 53.2 Do 14:30 H12

**Quantification of Complementarity in Multi-Qubit Systems** — •XINHUA PENG<sup>1,2</sup>, XIWEN ZHU<sup>2</sup>, DIETER SUTER<sup>1</sup>, JIANGFENG DU<sup>3</sup>, MAILI LIU<sup>2</sup>, and KELIN GAO<sup>2</sup> — <sup>1</sup>Fachbereich Physik, Universität Dortmund, 44221 Dortmund, Germany — <sup>2</sup>Wuhan Institute of Physics and Mathematics, Chinese Academy of Sciences, Wuhan 430071, P. R. China — <sup>3</sup>Hefei National Laboratory for Physical Sciences at Microscale and Department of Modern Physics, University of Science and Technology of China, Hefei, Anhui 230026, P.R. China

Complementarity was originally introduced as a qualitative concept for the discussion of properties of quantum mechanical objects that are classically incompatible. More recently, complementarity has become a quantitative relation between classically incompatible properties, such as visibility of interference fringes and "which-way" information, but also between purely quantum mechanical properties, such as measures of entanglement. We discuss different complementarity relations for systems of 2-, 3-, or n-qubits. Using nuclear magnetic resonance techniques, we have experimentally verified some of these complementarity relations in a two-qubit system. For three-qubit systems, we also propose an experimental scheme to verify some of the relevant complementarity relations for pure states.

MO 53.3 Do 14:45 H12

**Reducing Decoherence in Large Quantum Registers** — •MARKO LOVRIĆ, DIETER SUTER, and HANS GEORG KROJANSKI — Universität Dortmund, Fachbereich Physik, 44221 Dortmund, Germany

Decoherence appears to be the main limiting factor for the implementation of large (and therefore powerful) quantum computers. While it is generally expected that quantum registers consisting of many qubits will decay faster than smaller ones, the decoherence rates had never been measured for systems with more than 2 qubits. To obtain such data we measure the decay of model quantum registers consisting of up to several thousand nuclear spins. These states can be created by solid-state nuclear magnetic resonance (NMR) techniques. Our results indicate that the decoherence rates increase with the system size, but not as fast as generally expected. For successful operation of a quantum computer it will be essential to reduce decoherence processes. Several approaches have been proposed for decoupling the system from its environment. We have tested several techniques on our model quantum registers and found that it was possible to extend the decoherence time by more than an order of magnitude, independent of the size of the quantum register.

[1] H. G. Krojanski and D. Suter, Phys. Rev. Lett. 93, 090501 (2004)

MO 53.4 Do 15:00 H12

**The role of anharmonicity and coupling in molecular quantum computing** — •CAROLINE GOLLUB, ULRIKE TROPPMANN, and REGINA DE VIVIE-RIEDLE — LMU Department Chemie, Butenandt-Str. 11, 81377 München

Our approach of molecular quantum computing is based on eigenstates of vibrational normal modes of polyatomic molecules encoding the qubits. We analyze the effects of molecular characteristics on the structure of global quantum gates and the complexity of the resulting mechanisms systematically with the goal to judge a molecule's suitability for molecular quantum computing [1]. Decisive properties of molecular vibrations are the anharmonicity and the mode coupling. In a parametrized two-

dimensional model system we can tune these characteristic properties and explore their effects on quantum gates. We find that the interplay of the anharmonicity and the coupling is of prime importance and leads to two basic control mechanisms for all systems. The features of the global quantum gates are explained with characteristic transition frequencies, determined by the molecular parameters. The optimal time for the quantum gates and the limits to obtain simple structures are identified. Based on a universal set of optimized quantum gates we realized an efficient quantum fourier transformation [2].

[1] C. Gollub, U. Troppmann and R. de Vivie-Riedle. submitted to NJP

[2] U. Troppmann, C. Gollub and R. de Vivie-Riedle. submitted to NJP

MO 53.5 Do 15:15 H12

**Experimentally feasible quantum gates for MnBr(CO)<sub>5</sub>** — •BRIGITTE KORFF<sup>1</sup>, ULRIKE TROPPMANN<sup>2</sup>, KARL L. KOMPA<sup>1</sup>, and REGINA DE VIVIE-RIEDLE<sup>2</sup> — <sup>1</sup>MPI für Quantenoptik, Hans-Kopfermann-Str. 1, 85748 Garching — <sup>2</sup>LMU München, Department Chemie, Butenandt-Str. 11, 81377 München

In our concept for quantum computing qubits are encoded in vibrational normal modes of polyatomic molecules. Quantum gates are implemented by shaped femtosecond laser pulses. We adopt this concept to Manganese-pentacarbonyl-bromide (MnBr(CO)<sub>5</sub>) [1] a promising candidate in the mid-IR frequency range to connect theory and experiment. The 2D ab initio potential energy surface (PES) and the associated dipole vector surfaces spanned by the two strongest IR active modes are computed with DFT. Allowance for environmental effects makes the model flexible for variable experimental conditions. From the PES the vibrational eigenstates representing the qubit system are calculated. Laser pulses are optimized by multi target optimal control theory (MTOCT) to form a set of elementary global quantum gates. For all of them simply structured pulses with low pulse energies around 1 μJ and switching efficiencies above 99% could be obtained. Exemplarily for the CNOT gate we investigated the possible transfer to the experiment based on the mask function for pulse shaping in the frequency regime as well as decomposition into a train of gaussian subpulses.

[1] B. Korff et al, J. Chem. Phys. 123 (2005) 23xxxx

## Fachvortrag

MO 53.6 Do 15:30 H12

**Realization of Molecular Logic Gates by Femtosecond Multi-Photon Interaction** — •A. MATERNY, J. KONRADI, A.V. SCARIA and A.K. SINGH — International University Bremen, Bremen

Um ein logisches Gatter mit Hilfe eines Moleküls zu verwirklichen, können Mehrphotonenwechselwirkungen genutzt werden. Die Ordnung des nichtlinearen Prozesses entscheidet über die Komplexität, die Pulsdauer und moleküldynamische Parameter über die Geschwindigkeit des "Bausteins". In einer früheren Arbeit haben wir die Möglichkeit einer stimulierten Raman-Anregung (zwei Pulse) mit anschließender kohärenter anti-Stokescher Raman Streuung (CARS, Vierphotonenprozess) zur Verwirklichung eines Dreibit-Gatters ("Toffoli Gatter") diskutiert [1]. Hierbei werden Schwingungsmoden des Moleküls in Abhängigkeit von den beteiligten Laserpulsen genutzt und durch geeignete Kombinationen alle möglichen Gatterschaltungen (UND, ODER, usw.) verwirklicht. Unsere neuesten Arbeiten weisen auf eine Möglichkeit, diese logischen Gatter zu optimieren. Mit Hilfe der selbstlernenden Optimierungstechnik, können wir zwischen verschiedenen molekularen Schwingungsmoden hin- und herschalten [2]. In einer fs-CARS-Wechselwirkung bestimmt der elektronisch resonante oder nichtresonante Anregungsschritt (zwei Pulse, einer optimal geformt), welche spektrale Verteilung im Signal durch den Abfrageschritt erzeugt werden kann.

[1] A. N. Naumov, A. Materny, W. Kiefer, M. Motzkus, and A. M. Zheltikov, *Laser Phys.* **11**, 1319, (2001).

[2] J. Konradi, A.K. Singh, A. V. Scaria, and A. Materny, *J. Raman Spectrosc.*, in press (2006).

## MO 54 Cold Molecules II

Zeit: Donnerstag 14:00–15:45

Raum: H10

MO 54.1 Do 14:00 H10

**Ultracold atom-molecule collisions** — ●STEPHAN KRAFT<sup>1</sup>, PETER STAANUM<sup>1,2</sup>, JÖRG LANGE<sup>1</sup>, ROLAND WESTER<sup>1</sup>, and MATTHIAS WEIDEMÜLLER<sup>1</sup> — <sup>1</sup>Physikalisches Institut, Universität Freiburg, Freiburg, Germany — <sup>2</sup>Institut für Quantenoptik, Universität Hannover, Hannover, Germany

In the last years the field of ultracold molecules has developed rapidly and production and trapping of cold molecules has been demonstrated with different methods in several laboratories. The next step towards controlled ultracold chemistry is the investigation of interactions between ultracold atoms and molecules.

In this talk we report on the first observations of state-resolved ultracold collisions between atoms and molecules [1]. Cs and Cs<sub>2</sub> dimers in the triplet electronic ground state are trapped in a quasi electrostatic dipole trap. In the collisions internal excitation energy is converted into kinetic energy which leads to a loss of atoms and molecules from the dipole trap. From the measured loss rates we determine collision rate coefficients  $\beta \sim 10^{-10} \text{ cm}^3/\text{s}$  which are independent of the vibrational and rotational states indicating unitary limited cross sections. The collision rate coefficients are six times larger than the s-wave collision limit showing that s-, p- and d-waves contribute as expected at the collision temperature of 60  $\mu\text{K}$ .

[1] P. Staantum *et al.*, arXiv:physics/0509123 (Phys. Rev. Lett. in print)

MO 54.2 Do 14:15 H10

**Atom-molecule collisions in an optically trapped gas** — ●MARCEL MUDRICH<sup>1,2</sup>, NASSIM ZAHZAM<sup>2</sup>, THIBAUT VOGT<sup>2</sup>, DANIEL COMPARAT<sup>2</sup>, and PIERRE PILLET<sup>2</sup> — <sup>1</sup>Physikalisches Institut, Universität Freiburg — <sup>2</sup>Laboratoire Aimé Cotton, Orsay, France

Cold inelastic collisions between Cs atoms and Cs<sub>2</sub> molecules are investigated inside a CO<sub>2</sub> laser dipole trap [1,2]. Inelastic atom-molecule collisions are observed with a rate constant of  $\sim 9 \times 10^{-11} \text{ cm}^3\text{s}^{-1}$ , mainly independent of the populated molecular electronic ( $a^3\Sigma_u^+ / X^1\Sigma_g$ ) and rovibrational states. Storage times of pure atomic and molecular samples are essentially limited by rest gas collisions. The pure molecular rest-gas limited lifetime of up to 1 s is four times smaller than the atomic one, as observed in a pure magnetic trap. We estimate the inelastic molecule-molecule collision rate to be of the order of  $\sim 1 \times 10^{-11} \text{ cm}^3\text{s}^{-1}$ .

[1] N. Zahzam, T. Vogt, M. Mudrich, D. Comparat, P. Pillet, physics/0509197

[2] P. Staantum, S. D. Kraft, J. Lange, R. Wester, M. Weidemüller, physics/0509123

MO 54.3 Do 14:30 H10

**Collision Observed in a Supersonic Atomic-molecular Beam of K** — ●I. SHERSTOV, S. LIU, H. KNÖCKEL, and E. TIEMANN — Institut für Quantenoptik, Universität Hannover, Welfengarten 1, 30167 Hannover

We apply matter wave interferometry method implemented for Potassium molecules to investigate cold collision between Potassium atoms and molecules. Our goal is to interpret these observations with the interaction potential between K and K<sub>2</sub>.

We use supersonic expansion to create an atomic beam with a few percent of K<sub>2</sub> molecules diluted in it. K<sub>2</sub> molecules propagate within an atomic medium and hence gain some additional phase shift due to cold collisions with the atoms. By changing the properties of the medium (like exciting K atoms to a higher electronic state or varying the density of the atoms in the beam) a change of the phase and amplitude of the interference patterns is expected. By deflecting atoms out of molecular beam we were able to change the atomic density by one order of magnitude and observed a phase shift of the interference structure relating to a pressure shift in the order of 10 kHz for molecular transition of Potassium.

MO 54.4 Do 14:45 H10

**Experimental evidence for Efimov quantum states** — ●M. MARK<sup>1</sup>, T. KRAEMER<sup>1</sup>, P. WALDBURGER<sup>1</sup>, J.G. DANZL<sup>1</sup>, C. CHIN<sup>1,2</sup>, B. ENGESER<sup>1</sup>, A.D. LANGE<sup>1</sup>, K. PILCH<sup>1</sup>, A. JAAKKOLA<sup>1</sup>, H.-C. NAEGERL<sup>1</sup>, and R. GRIMM<sup>1,3</sup> — <sup>1</sup>Institut für Experimentalphysik, Universität Innsbruck, Technikerstr. 25, A-6020 Innsbruck — <sup>2</sup>James Franck Institute, Physics Department of the Univ. of Chicago, 5640 S. Ellis Ave. Chicago, Illinois 60637 USA — <sup>3</sup>Institut für Quantenoptik und Quanteninformation der Österreichischen Akademie der Wissenschaften, Otto-Hittmair-Platz 1, A-6020 Innsbruck

A landmark theoretical advance in few-body quantum physics is Efimov's prediction of weakly bound three-body states occurring close to a two-body scattering resonance. Among the amazing properties predicted for Efimov states is the existence of weakly bound trimer states even when the interaction does not support a weakly bound dimer state. Since the Efimov problem originally occurred 35 years ago in the context of nuclear matter, it has attracted great interest in many different areas of physics.

In my talk I will report on the observation of an "Efimov resonance" as a clear manifestation of an Efimov state. The resonance arises in the zero collision energy limit from the coupling of three free atoms to an Efimov trimer and shows up as a giant three-body loss feature when the two-body interaction is magnetically tuned near a Feshbach resonance. Our results confirm central theoretical predictions of Efimov physics and represent a starting point to explore the universal properties of resonantly interacting few-body systems [T. Kraemer *et al.*, publ. *subm.* (2005)].

MO 54.5 Do 15:00 H10

**Stark deceleration and trapping of OH radicals** — ●STEVEN HOEKSTRA, JOOP J. GILJAMSE, SEBASTIAAN Y.T. VAN DE MEERAKKER, and GERARD MEIJER — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195, Berlin

Over the last years our group has been developing methods to get improved control over the absolute velocity and the velocity spread of molecules in a molecular beam. With the Stark decelerator, a part of a molecular beam can be selected and transferred to any arbitrary velocity, producing bunches of state-selected molecules with longitudinal temperatures as low as a few mK.

We will report on the electrostatic trapping of ground state OH radicals. Typically 10<sup>5</sup> groundstate OH radicals are trapped for times up to 1.5 seconds at a temperature in the 50-500 mK range [PRL 94 23004 (2005)]. The long interaction time offered by the trap can be exploited to measure the radiative lifetime of long-lived excited states of a molecule [PRL 95 013003(2005)]. Furthermore, we have optimized the trap loading by using evolutionary strategies, resulting in an increase of the number of trapped molecules by 40%.

Recently we have performed the first inelastic scattering experiments using a Stark decelerated beam of polar molecules. Groundstate OH radicals are decelerated, and after collisions with a Xenon beam we measure the fraction of OH molecules in higher rotational states. The control we have over the beam of OH radicals enables us to tune the collision energy over the energetic threshold for inelastic scattering to these states.

MO 54.6 Do 15:15 H10

**Zeeman spectroscopy and magnetic trapping of CrH radicals** — ●JOOST M. BAKKER<sup>1,2</sup>, MICHAEL STOLL<sup>1,2</sup>, JENHEI CHENG<sup>3</sup>, TIMOTHY C. STEIMLE<sup>3</sup>, GERARD MEIJER<sup>2</sup>, and ACHIM PETERS<sup>1</sup> — <sup>1</sup>Humboldt Universität zu Berlin — <sup>2</sup>Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin — <sup>3</sup>Arizona State University, USA

The buffer gas loading and subsequent magnetic trapping of neutral molecules is a powerful tool for it provides samples of cold molecules with the highest densities known, while being applicable to a great variety of paramagnetic species. Metal-hydride molecules form an interesting class of molecules to study in such cold environments. Due to their complicated electronic structure, but still rather limited size, they form an appealing subject of study for quantum chemistry calculations. The possibility to buffer gas load these molecules and confine them inside a trap at high densities would directly allow for the study of their intermolecular collisional properties.

To investigate the applicability of magnetically trapping CrH molecules, we have studied the Zeeman effect of CrH radicals produced in a molecular beam. The measured Zeeman structure is complex, but can

theoretically well be described using an effective Hamiltonian treatment. Finally, the feasibility of buffer-gas loading of these interesting radicals is discussed.

MO 54.7 Do 15:30 H10

**LiCs molecules: High-resolution spectroscopy and applications to experiments with ultracold molecules** — ●P. STAANUM<sup>1,2</sup>, A. PASHOV<sup>3</sup>, H. KNÖCKEL<sup>2</sup>, E. TIEMANN<sup>2</sup>, S. D. KRAFT<sup>1</sup>, J. LANGE<sup>1</sup>, L. VOGEL<sup>1</sup>, C. GIESE<sup>1</sup>, B. MÜLLER<sup>1</sup>, R. WESTER<sup>1</sup>, and M. WEIDEMÜLLER<sup>1</sup> — <sup>1</sup>Physikalisches Institut, Universität Freiburg, Hermann-Herder-Strasse 3, 79104 Freiburg — <sup>2</sup>Institut für Quantenoptik, Universität Hannover, Welfengarten 1, 30167 Hannover — <sup>3</sup>Department of Physics, Sofia University, 5 James Bourchier Blvd., 1164 Sofia, Bulgaria

With the recent developments in formation and trapping of ultracold molecules new possibilities for experimental studies within the

field of ultracold chemistry have emerged. Ultracold atom-molecule and molecule-molecule collisions can be studied in an optical dipole trap as it was recently done for Cs + Cs<sub>2</sub> collisions (P. Staantum *et al.*, arXiv:physics/0509123 and N. Zahzam *et al.* arXiv:physics/0509197. To appear in Phys. Rev. Lett.). For heteronuclear molecules, studies of ultracold reactive collisions like LiCs+Cs ↔ Li+Cs<sub>2</sub> have become feasible.

We aim at formation of LiCs molecules by photoassociation from mixed Li-Cs cold atom samples. A detailed understanding of LiCs photoassociation as well as state-dependent collision processes requires accurate LiCs potential curves. We have obtained such curves for the X<sup>1</sup>Σ<sup>+</sup> and a<sup>3</sup>Σ<sup>+</sup> electronic ground states as well as the B<sup>1</sup>Π and D<sup>1</sup>Π excited states through high-resolution laser-induced fluorescence Fourier-transform spectroscopy. We present here our spectroscopic results on LiCs and their application, as well as the status of our work on formation of LiCs by photoassociation and experiments with these molecules.

## MO 55 Poster: Collisions and Energy Transfer

Zeit: Donnerstag 16:30–18:30

Raum: Labsaal

MO 55.1 Do 16:30 Labsaal

**Crossed-beam imaging of ion-molecule reaction dynamics** — ●J. MIKOSCH<sup>1,2</sup>, S. TRIPPEL<sup>1</sup>, R. BERHANE<sup>1</sup>, R. OTTO<sup>1</sup>, D. SCHWALM<sup>2</sup>, M. WEIDEMÜLLER<sup>1</sup>, and R. WESTER<sup>1</sup> — <sup>1</sup>Physikalisches Institut, Universität Freiburg, 79104 Freiburg — <sup>2</sup>Max-Planck-Institut für Kernphysik, 69117 Heidelberg

We present a new ion-molecule crossed-beam experiment with a velocity map imaging detector [1], which allows for kinematically complete studies of ion-molecule reactions at very low relative collision energies (< 1eV). With this system we aim at an improved understanding of the quantum dynamics of fundamental anion-molecule reactions, a model system being the nucleophilic substitution reaction Cl<sup>-</sup> + CH<sub>3</sub>I → I<sup>-</sup> + CH<sub>3</sub>Cl [2]. We are particularly interested in the vibrational state-to-state reaction dynamics and the relevance of spectator modes on the cross section [3]. Furthermore, experiments with laser-aligned molecules are projected, which open the possibility to study reactive scattering in strong laser fields.

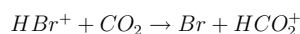
To unravel the kinetic energy and angular distributions from measured images we have set up a Monte Carlo reconstruction algorithm. As an experimental benchmark we have studied the charge transfer reaction Ar<sup>+</sup> + N<sub>2</sub> → Ar + N<sub>2</sub><sup>+</sup>.

[1] A. T. J. B. Eppink and D. H. Parker, Rev. Sci. Instrum. **68**, 3477 (1997) [2] L. Sun, K. Song, W. Hase, Science **296**, 875 (2002) [3] C. Hennig and S. Schmatz, Phys. Chem. Chem. Phys. **7**, 1100 (2005)

MO 55.2 Do 16:30 Labsaal

**Ionen-Molekül-Reaktionen zustandsselektierter Bromwasserstoff-Ionen** — ●STEFAN ATHENSTÄDT und KARL-MICHAEL WEITZEL — Philipps Universität Marburg, FB Chemie, Hans-Meerweinstr., 35032 Marburg

Ionen-Molekül-Reaktionen spielen sowohl in technischen Prozessen, z.B. in der Plasmachemie, als auch im interstellaren Raum eine wichtige Rolle. Vor allem Reaktionen von zustandsselektierten Molekülionen haben in den vergangenen Jahren große Aufmerksamkeit auf sich gezogen. Von besonderem Interesse hierbei ist die Fragestellung, ob Reaktionen durch Wahl definierter Rotationszustände kontrolliert werden können.



Wir beschreiben in diesem Beitrag Untersuchungen der Protonentransferreaktion zustandsselektierter Bromwasserstoff-Ionen mit neutralem Kohlendioxid.

Die Molekül-Ionen werden rotationsselektiv über resonanzverstärkte Mehrphotonenionisation (REMPI) erzeugt [1]. Reaktion (1) erfolgt dann innerhalb eines Drahtvierpols, welcher als Ionenführungssystem dient. Die Produktverteilung wird als Funktion der Rotationsquantenzahl des HBr<sup>+</sup>-Ions analysiert. Erste Messungen deuten auf eine starke Abnahme der Reaktionsgeschwindigkeit bei zunehmender Rotationsanregung hin. [1] Martin Penno, Karl-Michael Weitzel, Z. Phys. Chem. **218** (2004), 311.

MO 55.3 Do 16:30 Labsaal

**Collision-induced rototranslational absorption in compressed methane gas** — ●MICHAEL BUSER<sup>1</sup> and LOTHAR FROMMHOLD<sup>2</sup> — <sup>1</sup>Universität Ulm — <sup>2</sup>University of Texas at Austin

Transient collisional complexes of two or more atoms or molecules acquire properties which do not exist in the non-interacting constituents. Collision-induced, rototranslational absorption spectra in even non-polar molecules arise. Such spectra were calculated for methane molecules numerically, based on a theoretical dipole function which accounts for the long-range induction mechanisms: multipolar induction and induction by dispersion and exchange forces. By comparing the computed results to existing measurements, a sizeable absorption defect at virtually all frequencies can be observed. The occurrence in different methane gas mixtures like CH<sub>4</sub>-N<sub>2</sub>, CH<sub>4</sub>-H<sub>2</sub>, CH<sub>4</sub>-He and CH<sub>4</sub>-CH<sub>4</sub> considered in this work suggests the presence of an addition induction mechanism, which seems to be related to collisional distortion of the tetrahedral frame of the unperturbed CH<sub>4</sub> molecule.

MO 55.4 Do 16:30 Labsaal

**Präzise Bestimmung atomarer Wechselwirkungspotentiale durch die Laseranregung von Stoßpaaren** — ●ANDRE GRIMPE<sup>1</sup>, CRISTINA FIGL<sup>1</sup>, RALF GOLDSTEIN<sup>1</sup>, JOACHIM GROSSER<sup>1</sup>, OLAF HOFFMANN<sup>1</sup>, ÖRSAN YÜKSEK<sup>1</sup> und FRANK REBENTROST<sup>2</sup> — <sup>1</sup>Institut für Gravitationsphysik, Hannover — <sup>2</sup>Max-Planck-Institut für Quantenoptik, Garching

Bei der Laseranregung von Stoßpaaren mit differentiellen Nachweis der Stoßprodukte entstehen Interferenzstrukturen, die als empfindliche Sonde für die Potentiale dienen können. Wir haben die Systeme

Li+He, Ne, H<sub>2</sub>, D<sub>2</sub>, Na+Ne, Ar, Xe, K+Ar und Ca+Ar untersucht. Für das KAr-System haben wir die abstoßenden Zweige der X- und B-Potentiale bis 1000 cm<sup>-1</sup> über der Asymptote mit Genauigkeiten zwischen 2 und 10 cm<sup>-1</sup> bestimmt. Für die anderen Systeme sind wir in der Lage, Aussagen über die Genauigkeit spektroskopischer oder quantenchemischer Potentiale mit einer Empfindlichkeit von wenigen cm<sup>-1</sup> zu machen.

MO 55.5 Do 16:30 Labsaal

**Kontrolle und Abbildung atomarer und molekularer Stoßvorgänge durch polarisierte Laserstrahlung** — ●JOACHIM GROSSER, CRISTINA FIGL, RALF GOLDSTEIN, ANDRÉ GRIMPE, OLAF HOFFMANN und FRANK REBENTROST — Arbeitsgruppe Atomare Prozesse des Institutes für Gravitationsphysik, Universität Hannover

Stoßpaare wie Na+Ne oder Na+C<sub>2</sub>H<sub>2</sub> werden während des Stoßes durch Laserlicht angeregt und nach dem Stoß winkelaufgelöst nachgewiesen. Mit der Polarisation der Laserstrahlung kann die relative Amplitude und Phase verschiedener Prozesswege kontrolliert und dadurch der differentielle Querschnitt manipuliert werden. Darüber hinaus ergibt die Polarisationsabhängigkeit der Signale ein geometrisches Bild des Stoßkomplexes.

MO 55.6 Do 16:30 Labsaal

**Nichtadiabatische Elementarprozesse in Atom-Atom- und Atom-Molekül-Stößen** — ●JOACHIM GROSSER, CRISTINA FIGL, RALF GOLDSTEIN, ANDRÉ GRIMPE, OLAF HOFFMANN und FRANK REBENTROST — Arbeitsgruppe Atomare Prozesse des Institutes für Gravitationsphysik, Universität Hannover

Wir messen die Übergangswahrscheinlichkeiten zwischen atomaren Feinstrukturniveaus im Ausgangskanal von Stoßprozessen. Durch Laseran-

regung wird das Stoßpaar während des Stoßes in einem bestimmten elektronischen Zustand präpariert. Die Zustandsbesetzung nach dem Stoß zeigt unmittelbar die nichtadiabatische Übergangswahrscheinlichkeit. Theoretische Rechnungen werden auf der Grundlage quantenchemischer oder experimentell bestimmter Potentiale durchgeführt und ergeben teilweise eine ausgezeichnete Übereinstimmung mit dem Experiment.

MO 55.7 Do 16:30 Labsaal

**Dissociative electron attachment to gas phase explosives** — ●PHILIPP SULZER<sup>1</sup>, FLAMINIA RONDINO<sup>2</sup>, DAVID KILGOUR<sup>3</sup>, VERENA GRILL<sup>1</sup>, SYLWIA PTASINSKA<sup>1</sup>, STEPHAN DENIFL<sup>1</sup>, PAUL SCHEIER<sup>1</sup>, and TILMANN D. MÄRK<sup>1</sup> — <sup>1</sup>Institut für Ionenphysik, Leopold-Franzens-Universität Innsbruck, Technikerstr. 25, A 6020 Innsbruck — <sup>2</sup>Università di Roma, La Sapienza, Dipartimento di Chimica — <sup>3</sup>Defence Science and Technology Laboratory (Dstl), Fort Halstead, Detection Technology Department, Fort Halstead, Sevenoaks, Kent, TN14 7BP

Mass spectrometry is a potentially useful technology for the detection of explosives in security screening applications. Dissociative electron attachment is a resonant process and leads to the formation of (fragment) anions only at specific electron energies. The positions of the resonances depend strongly on the composition and structure of the neutral precursor molecule; thereby this dependence could provide an unambiguous identification of the explosive. In this contribution we present the attachment cross sections of all studied major product anions formed by free electron attachment to various gas phase explosives utilizing a high resolution hemispherical electron monochromator.

This work is partly supported by the FWF, Wien, the EU Commission, Brussels and the UK Ministry of Defence (MOD) through the Defence Science and Technology Laboratories (Dstl) contract RD031-011213 as

part of the Electronics Systems Research Programme.

MO 55.8 Do 16:30 Labsaal

**Dissociative recombination of  $H_3^+$ : evidence for nuclear spin effects** — ●HOLGER KRECKEL<sup>1</sup>, MICHAEL MOTSCH<sup>1</sup>, JOCHEN MIKOSCH<sup>1,2</sup>, JURAJ GLOSİK<sup>3</sup>, RADEK PLASIL<sup>3</sup>, SIMON ALTEVOGT<sup>1</sup>, VOLA ANDRIANARIJAONA<sup>1</sup>, HENRIK BUHR<sup>1</sup>, JENS HOFFMANN<sup>1</sup>, LUTZ LAMMICH<sup>1</sup>, MICHAEL LESTINSKY<sup>1</sup>, IFTACH NEVO<sup>4</sup>, STEFFEN NOVOTNY<sup>1</sup>, DMITRY A. ORLOV<sup>1</sup>, HENRIK B. PEDERSEN<sup>1</sup>, FRANK SPRENGER<sup>1</sup>, JONATHAN TOKER<sup>4</sup>, ROLAND WESTER<sup>2</sup>, DIETER GERLICH<sup>5</sup>, DIRK SCHWALM<sup>1</sup>, ANDREAS WOLF<sup>1</sup>, and DANIEL ZAJFMAN<sup>1,4</sup> — <sup>1</sup>Max-Planck-Institut für Kernphysik, D-69117 Heidelberg, Germany — <sup>2</sup>Physikalisches Institut, Universität Freiburg, 79104 Freiburg, Germany — <sup>3</sup>Faculty of Mathematics and Physics, Charles University Prague, Czech Republic — <sup>4</sup>Department of Particle Physics, Weizmann Institute of Science, Rehovot, 76100, Israel — <sup>5</sup>Institut für Physik, Technische Universität, 09107 Chemnitz, Germany

The dissociative recombination (DR) of  $H_3^+$  is one of the most important processes in the chemical networks of cold interstellar clouds, and still subject to a long-standing controversy regarding its rate coefficient at Kelvin temperatures.

We have performed a high resolution  $H_3^+$  DR measurement at the TSR storage ring, employing a cryogenic 22-pole ion trap at 13 K to precool the ions by buffer gas collisions to their two lowest rotational states. To lower the transversal electron temperature to 6 K and improve the resolution, a new photocathode electron source in the TSR electron target has been applied. Furthermore first evidence for a nuclear spin effect in the DR process was found by using para- $H_2$  gas in the ion source.

## MO 56 Poster: Molecular Clusters

Zeit: Donnerstag 16:30–18:30

Raum: Labsaal

MO 56.1 Do 16:30 Labsaal

**Hochauflösende Spektroskopie von Methan-Dimer im Bereich der  $\nu_4$ -Schwingung bei 1300  $cm^{-1}$**  — ●GERHARD SCHWAAB, ABDULLAH HAMDAN und MARTINA HAVENITH — Physikalische Chemie II, Ruhr-Universität Bochum, D-44780 Bochum

Spektren von Methan-Dimer ( $CH_4$ )<sub>2</sub> im Bereich von 1300  $cm^{-1}$  wurden mit Hilfe eines hochauflösenden Bleisalz-Diodenlaser-Spektrometers aufgenommen. Es besteht aus einer wahlweise kontinuierlich oder gepulst betriebenen 5 cm × 5  $\mu m$  Schlitzdüse und einem computergesteuerten Bleisalz-Diodenlaser. Durch eine Herriott-Zelle wird der Absorptionsweg auf bis zu 180 cm verlängert. Damit ergibt sich eine Nachweisempfindlichkeit  $\frac{\Delta I}{I_0}$  von  $10^{-5}$  –  $10^{-6}$ .

Zur Unterscheidung von Methan-Dimer und anderen Komplexen, z.B. Ar –  $CH_4$  wurde Methan alternativ mit Ar und mit He-Ne koexpandiert. Ein Teil der vermessenen Linien konnte den  $^R P_0$ -,  $^Q R_0$ - und  $^R Q_0$ -Zweigen des R(0)-Übergangs des dreifach entarteten  $\nu_4$ -Schwingungszustandes von Methan zugeordnet werden. ( $CH_4$ )<sub>2</sub> zeigt, ähnlich zu Ar –  $CH_4$  und Kr –  $CH_4$  eine starke Corioliswechselwirkung zwischen den K=0 und K=1<sup>+</sup> Zuständen des angeregten Vibrationszustandes. Aus der Corioliskopplungskonstanten konnte ein effektiver Drehimpuls  $j^* = 0.95$  für den angeregten Zustand abgeleitet werden. Dies entspricht etwa dem Wert für Ne- $CH_4$  (=0.97) und legt eine weitgehend freie Rotation der Methan-Monomere im angeregten Zustand nahe.

MO 56.2 Do 16:30 Labsaal

**Winkelaufgelöste fs-Photoelektronenspektroskopie an Na-Clustern** — ●CHRISTIAN HOCK, CHRISTOF BARTELS, JÖRG SCHWÖBEL, RAPHAEL KUHNEN, ABDOLLAH MALAKZADEH, PASCAL DIDIER und BERND VON ISSENDORFF — Institut für Physik, Universität Freiburg, Stefan-Meier-Straße 19, 79104 Freiburg

Ein Bildspektrometer zur Messung von winkelaufgelösten Photoelektronenspektren an Clustern wurde aufgebaut. Erste Messungen mit fs-Laserpulsen (400 nm, 100 fs) an positiven und negativen Natrium-Clusterionen wurden durchgeführt, um frühere Ergebnisse zur Emission thermischer Elektronen aus einem hochangeregten Elektronengas [1] zu überprüfen. Wie erwartet, zeigt sich eine perfekt isotrope Winkelverteilung der thermischen Photoelektronen.

Durch Ein- oder Mehrphotonenabsorption kann eine kollektive Anregung des Elektronengases (Plasmon) stattfinden. Die lokale Feldverstärkung sollte in diesem Falle zur Emission von Elektronen

mit einer stark anisotropen Winkelverteilung führen, die allerdings immer von der isotropen Verteilung thermischer Elektronen überlagert wird. Messungen mit kurzen Laserpulsen (< 50 fs) zum Nachweis dieses Effekts sind in Vorbereitung.

[1] Schlipper et al., Appl. Phys. A 72, 255–259 (2001)

MO 56.3 Do 16:30 Labsaal

**Probing the Stepwise Solvation of the Sulfate Dianion: Gas Phase Infrared Spectroscopy of  $SO_4^{2-} \cdot (H_2O)_n$  Clusters (n=3–24)** — ●GABRIELE SANTAMBROGIO<sup>1</sup>, JIA ZHOU<sup>2</sup>, MATHIAS BRÜMMER<sup>1</sup>, DAVE MOORE<sup>2</sup>, LUDGER WÖSTE<sup>1</sup>, GERARD MEIJER<sup>3</sup>, DANIEL M. NEUMARK<sup>2,4</sup>, and KNUT R. ASMIS<sup>3</sup> — <sup>1</sup>Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, D 14195 Berlin, Germany — <sup>2</sup>Department of Chemistry, University of California, Berkeley, CA 94720, USA — <sup>3</sup>Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin, Germany — <sup>4</sup>Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

Hydrated sulfate dianions are of paramount importance in diverse branches of science. However, a microscopic, molecular level understanding of the nature of the solute-solvent interaction as well as the composition of the solvation shell has not yet been achieved. Here we report the first gas phase infrared spectra of multiple charged anions in general, namely of mass-selected  $SO_4^{2-} \cdot (H_2O)_n$  dianions (n=3–24) employing the infrared multiple photon dissociation technique in combination with radiation from the free electron laser FELIX. The infrared spectra (550–1800  $cm^{-1}$ ) were measured in the region of the stretching and bending modes of the sulfate core as well as characteristic intra- and intermolecular water modes, allowing an unprecedented, atomic level insight into structure of the complex as well as the nature and strength of the underlying hydrogen bonding interaction.

MO 56.4 Do 16:30 Labsaal

**Pump-Probe-Spectroscopy of  $C_{60}^-$  and  $C_{70}^-$  using Hollow-Capillary-Compressor** — ●ABDOLLAH MALAKZADEH, PASCAL DIDIER, CHRISTINE WEHRSTEIN, RAPHAEL KUHNEN, and BERND V. ISSENDORFF — Physikalisches Institut, Universität Freiburg, Stefan-Meier-Str. 21, 79104 Freiburg

The electronic valence structure of fullerenes is determined by the delocalized  $\pi$ -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  $C_{60}^-$  and  $C_{70}^-$  irradiated by fs-laserpulses multiphoton-electron detachment processes have been observed. In order to study the pulse length dependence of this effects the pulses of the amplified 100fs Ti:Sa-lasersystem have been shortened by spectral broadening in hollow capillary waveguides. The compressor gives pulses of 25fs at 200 $\mu$ J pulse energy centered at 790nm wavelength. The short pulses increase the higher order effects in the photoelectron-spectra.

MO 56.5 Do 16:30 Labsaal

**Reactivity and Infrared Spectroscopy of mass selected vanadium oxide cluster ions** — ●MATHIAS BRÜMMER<sup>1</sup>, JENS DÖBLER<sup>2</sup>, SARA FONTANELLA<sup>1</sup>, GABRIELE SANTAMBROGIO<sup>1</sup>, JOACHIM SAUER<sup>2</sup>, LUDGER WÖSTE<sup>1</sup>, and KNUT ASMIS<sup>3</sup> — <sup>1</sup>Freie Universität Berlin, Institut für Experimentalphysik, Arnimallee 14, 14195 Berlin — <sup>2</sup>Humboldt Universität Berlin, Institut für Chemie, Unter den Linden 6, 10099 Berlin — <sup>3</sup>Fritz Haber Institut der Max Planck Gesellschaft, Abteilung Molekülphysik, Faradayweg 4-6, 14195 Berlin

Despite the enormous importance of transition metal oxides based catalysts very little is known about their microscopic details. Vanadium oxides catalyze the oxidation of SO<sub>2</sub> to SO<sub>3</sub>, an important step in the production of sulfuric acid. We performed experiments in which we spectroscopically followed the reaction of vanadium oxide anions (V<sub>2</sub>O<sub>5</sub>)<sub>n</sub><sup>-</sup>, for n=2 to 4, with sulfur dioxide via infrared multiphoton photodissociation. All spectra show absorption bands in both the vanadyl and the V-O-V region of the spectrum. Differences in the spectra of the bare vanadium oxide anions were interpreted as a consequence of size-induced localization of the extra electron. The spectra measured after SO<sub>2</sub> absorption indicate a chemisorption of sulfur dioxide. Recent calculations on [V<sub>4</sub>O<sub>10</sub>SO<sub>2</sub>]<sup>-</sup> indicate that here SO<sub>2</sub> is inserted into the vanadium oxide cage. For the larger systems the vanadyl bond on which the extra electron is located seems to be the active site. Here a chemical reaction between the vanadyl-oxygen and SO<sub>2</sub> to SO<sub>3</sub> is expected.

## MO 57 Poster: Cold Molecules

Zeit: Donnerstag 16:30–18:30

Raum: Labsaal

MO 57.1 Do 16:30 Labsaal

**Towards laser induced reactions of negative ions in a cold 22-pole ion trap** — ●S. TRIPPEL, R. BERHANE, R. OTTO, J. MIKOSCH, M. WEIDEMÜLLER, and R. WESTER — Physikalisches Institut, Universität Freiburg, 79104 Freiburg

Radio-frequency traps are widely used to store and investigate ions. In the last decade it became clear, that collisional cooling of vibrations and rotations of molecular ions in a rf-trap requires high order multipole fields. Therefore we employ a 22-pole rf-ion trap to prepare molecular ions in certain rovibrational states and to investigate the influence of this preparation on chemical reactions such as OH<sup>-</sup> + H<sub>2</sub> → H<sub>2</sub>O + H<sup>-</sup>. This reaction is predicted to be exoergic only if the OH<sup>-</sup> ion populates a vibrational level  $v \geq 2$ . Exciting one of these levels with laser light will induce a reaction and allows for a precise spectroscopy of the involved levels and a diagnostics of the rotational level population of OH<sup>-</sup> in the trap [1]. Currently a 10K cooling system for the trap is constructed to cool OH<sup>-</sup> to a single rotational state. The status of the experiment and the next steps to measure rotational state-specific collision rates at low temperatures will be described. Simulations based on the Debye-Hückel model are presented which yield predictions for the radial distribution of the trapped ions. Furthermore, the design for a new micro-ion-trap, developed in cooperation with the Institute of Microfabrication at the University of Freiburg, is presented.

[1] J. Mikosch, H Kreckel, R. Wester, R. Plašil and J. Glosík, D. Gerlich, D. Schwalm and A. Wolf, J.Chem.Phys. **121**, 11030 (2004)

MO 57.2 Do 16:30 Labsaal

**Towards High Precision Spectroscopy of Ultracold Molecular Hydrogen Ions in a Linear Radiofrequency Trap** — ●BERNHARD ROTH, HEINER DAERR, JEROEN KOELEMELJ, ALEXANDER NEVSKY, and STEPHAN SCHILLER — Heinrich-Heine-Universität Düsseldorf

We have cooled the molecular hydrogen ions H<sub>2</sub><sup>+</sup> and H<sub>3</sub><sup>+</sup> and all their deuterated isotopomers (HD<sup>+</sup>, H<sub>2</sub>D<sup>+</sup>, HD<sub>2</sub><sup>+</sup>, D<sub>3</sub><sup>+</sup>, D<sub>2</sub><sub>2</sub><sup>+</sup>, and D<sup>+</sup>) to translational temperatures in the 10 millikelvin range, by sympathetic cooling with laser-cooled beryllium ions, stored in a linear radiofrequency trap. The largest ion crystals contained more than 3000 well localized hydrogen molecules and up to 6000 <sup>9</sup>Be<sup>+</sup> ions. The mass ratio  $m_{sc}/m_{lc}$  of 0.2 between sympathetically cooled H<sub>2</sub><sup>+</sup> and laser-cooled Be<sup>+</sup> ions is the smallest achieved so far. The different ion species were detected mass-selectively by excitation of their trap oscillation modes. The observed crystal structures agree well with results from molecular dynamics simulations which were also used to deduce an indirect upper limit for their translational temperature.

Ultracold hydrogen molecules have the potential for precision tests of molecular structure theory, tests of Lorentz invariance, and measurements of electron and nuclear masses and their time variation. In particular, HD<sup>+</sup> ions are of interest because they have dipole-allowed transitions.

Currently, we are performing 1+1 REMPI spectroscopy of ultracold HD<sup>+</sup>. The ro-vibrational overtone transitions  $v = 0 \rightarrow v = 4$  in HD<sup>+</sup> at

1.4  $\mu$ m will be excited and subsequently the excited molecules will be dissociated using an 266 nm-UV-laser. The disappearance rate of ultracold HD<sup>+</sup> from the trap will be detected.

MO 57.3 Do 16:30 Labsaal

**Sympathetic cooling of singly-protonated polyatomic molecules to sub-Kelvin temperatures** — ●BERNHARD ROTH, CHAOBO ZHANG, DAVID OFFENBERG, ALEXANDER WILSON, ALEXANDER OSTENDORF, and STEPHAN SCHILLER — Heinrich-Heine-Universität Düsseldorf

Alexa Fluor 350, a fluorescent dye molecule of mass 410 AMU, has been transferred from an electro spray ionisation (ESI) source to a linear Paul trap, via a 2-m long octopole ion guide. Around 2300 laser-cooled <sup>138</sup>Ba<sup>+</sup> ions in a Coulomb crystal were used to sympathetically cool approximately 600 Alexa Fluor ions to below 100 mK. The sympathetically cooled ions are identified by monitoring the resonance fluorescence of the <sup>138</sup>Ba<sup>+</sup> ions during secular excitation. Observations are well described by molecular dynamic simulations, which are used to determine the number of ions, their spatial distribution and translational temperature. The ESI technique should allow many different kinds of molecules to be transferred for trapping and sympathetic cooling; of particular interest may be molecules of very high mass and those of biological relevance, indeed, Alexa Fluor 350 is usually used in biological studies for protein labelling.

MO 57.4 Do 16:30 Labsaal

**A microdecelerator for polar molecules** — ●SAMUEL A. MEEK, HENDRICK L. BETHLEM, HORST CONRAD, and GERARD MELJER — Fritz-Haber-Institut der MPG, Faradayweg 4-6, 14195 Berlin

By utilizing the forces that polar molecules experience in inhomogeneous electric fields, a variety of molecular-optical elements have been experimentally demonstrated. The electrode dimensions used for previous experiments have been relatively large. To reach sufficiently high electric fields with electrodes which are several mm apart, potentials of tens of kV need to be applied. We have recently demonstrated that modest voltage differences applied to  $\mu$ m-sized electrodes produce equally high electric fields [1]. Here, we present design and trajectory calculations for an electrostatic decelerating and trapping device consisting of a periodic array of 1000 microstructured linear electrodes deposited on a planar insulating substrate. Alternating electric potentials are applied to the electrodes in such a way that local electric field minima occur above the electrode plane. Application of harmonic waveforms to periodic groups of 6 electrodes allows us to steer the resulting periodic minima along the array in a continuous manner without changing their distance above the electrodes. Deceleration is achieved by linearly reducing the frequency of the applied waveforms. The molecule of choice for these experiments is a<sup>3</sup>Π<sub>1</sub> CO. Since the lifetime of this metastable state is about 3 ms, the molecules can be detected via their spontaneous emission. Trajectories covering a whole range of initial conditions in phase space have been



calculated to estimate the stable region during deceleration.

[1] S.A. Schulz et al, Phys.Rev.Lett. 93, 020406 (2004)

MO 57.5 Do 16:30 Labsaal

**Erste Stark-Abbremsung von SO<sub>2</sub>** — ●S. JUNG<sup>1</sup>, G. MEIJER<sup>2</sup>, E. TIEMANN<sup>1</sup> und CH. LISDAT<sup>1</sup> — <sup>1</sup>Institut für Quantenoptik, Universität Hannover, Welfengarten 1, 30167 Hannover — <sup>2</sup>Fritz-Haber-Institut, Faradayweg 4-6, 14195 Berlin

Kalte Schwefeldioxid Moleküle bieten interessante Möglichkeiten für Experimente, so zum Beispiel die schwellnahe Photodissoziation in die Fragmente SO + O. Kaltes SO<sub>2</sub> sollte aufgrund seines Dipolmomentes grundsätzlich mit einem Stark-Abbremsers aus einem Molekülstrahl erzeugt werden können. Allerdings ist die Masse von SO<sub>2</sub> verglichen mit anderen Molekülen in Abbremsexperimenten groß, was zu einer hohen kinetischen Anfangsenergie führt und lange, vielstufige Abbremsstrecken erfordert.

Wir haben einen Abbremsers für Moleküle in schwachfeldsuchenden Zuständen realisiert, der aus 140 Stufen besteht. Dieser ermöglicht, die kinetische Energie der SO<sub>2</sub> Moleküle um 42% zu reduzieren. Basierend auf diesen Ergebnissen wird derzeit ein verlängerter Aufbau mit mehr als 320 Stufen realisiert, der Teilchengeschwindigkeiten nahe null erzeugen kann. Diese Moleküle sollen dann in einer elektrostatischen Falle gefangen werden.

MO 57.6 Do 16:30 Labsaal

**Spektroskopie von NaK** — ●A. STEIN, A. GERDES, ST. FALKE, H. KNÖCKEL und E. TIEMANN — Institut für Quantenoptik, Universität Hannover, Welfengarten 1, 30167 Hannover

Die Untersuchung langreichweitiger Wechselwirkungen zwischen einem Kalium- und einem Natriumatom ist für Zweielementfallen von herausragender Bedeutung. Die Streulängen der heteronuklearen Stöße sollen mittels molekülspektroskopischer Experimente gewonnen werden. Große Bedeutung kommt dabei den hoch angeregten Vibrationszuständen der elektronischen Grundzustände X<sup>1</sup>Σ<sup>+</sup> und a<sup>3</sup>Σ<sup>+</sup> zu [1]. Diese sollen mittels Mehrphotonenanregung in einem kontinuierlichen NaK-Strahl laserspektroskopisch hochauflösend untersucht werden. Mit einem vergleichbaren Aufbau wurden in unserer Arbeitsgruppe bereits die Streueigenschaften von kaltem Natrium untersucht [2]. Zur Charakterisierung der als Zwischenzustände benutzen angeregten elektronischen Zustände werden Voruntersuchungen mit Heatpipe und Fouriertransformenspektrometrie von laserinduzierter Fluoreszenz durchgeführt. Der Stand der Aufbauarbeiten einer Strahlapparatur und der Voruntersuchungen von NaK werden vorgestellt.

[1] J. Venturi et al. J. Phys. B **34**, 4339, 2001.

[2] Chr. Samuelis et al., Phys. Rev. A **63** 012710, 2001.

MO 57.7 Do 16:30 Labsaal

**A two-species experiment for ultracold chemistry** — ●LEIF VOGEL<sup>1</sup>, CHRISTIAN GIESE<sup>1</sup>, BENJAMIN MÜLLER<sup>1</sup>, JÖRG LANGE<sup>1</sup>, STEPHAN KRAFT<sup>1</sup>, PETER STAANUM<sup>1,2</sup>, ROLAND WESTER<sup>1</sup>, and MATTHIAS WEIDEMÜLLER<sup>1</sup> — <sup>1</sup>Physikalisches Institut Universität Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg — <sup>2</sup>Institut für Quantenoptik, Universität Hannover, Welfengarten 1, 30167 Hannover

The study of atom-molecule interactions at very low temperature has opened possibilities in the field of ultracold chemistry. In this context we are particularly interested in the exchange reaction LiCs + Cs ↔ Li + Cs<sub>2</sub>.

We form Cs<sub>2</sub> by photoassociation in a quasi electrostatic optical trap and aim at forming LiCs in the same way. In our recent experiments Cs-Cs<sub>2</sub> collision rates at ultracold temperatures were found to be largely independent of their rotational and vibrational excitation[1]. In contrast, for ultracold exchange reactions the molecular binding energies and reaction barriers are expected to play an important role. We present our experiment aiming at the efficient production of cold molecules at high densities and discuss the prospects of studying state-resolved reactive scattering in the quantum collision regime.

[1] P. Staantum et al. arXiv:physics/0509123 (Phys. Rev. Lett. in press)

MO 57.8 Do 16:30 Labsaal

**Cold Collisions of KRb studied by High Resolution Molecular Spectroscopy** — ●A. GERDES<sup>1</sup>, O. DOCENKO<sup>2</sup>, M. TAMANIS<sup>2</sup>, R. FERBER<sup>2</sup>, A. PASHOV<sup>3</sup>, H. KNÖCKEL<sup>1</sup>, and E. TIEMANN<sup>1</sup> — <sup>1</sup>Institut für Quantenoptik, Universität Hannover, Welfengarten 1, 30167 Hannover — <sup>2</sup>Department of Physics and Institute of Atomic Physics and Spectroscopy, University of Latvia, Rainis Boulevard 19, LV 1586 Riga, Latvia — <sup>3</sup>Department of Physics, Sofia University, 5 James Bourchier blvd, 1164 Sofia, Bulgaria

Detailed knowledge of the electronic ground states of KRb allows for the description of cold collisions, which are governing the dynamics of ultracold K-Rb mixtures in two species traps. We record the relevant spectroscopic data with a Fourier transform spectrometer by recording laser induced fluorescence of KRb. The closer the observed levels lie at the ground state asymptote, the more relevant is the information for derivation of the scattering length or Feshbach resonance positions. The spectroscopic data allow a precise determination of the potential energy curves for singlet and triplet ground state, and together with data input from recent Feshbach resonance measurements [1] also a precise description of the long range properties for all hyperfine asymptotes becomes derivable. The status of the analysis will be reported.

[1] Francesca Ferlaino, et al., arXiv:cond-mat/0510630 v1 24 Oct 2005

MO 57.9 Do 16:30 Labsaal

**High Resolution Spectroscopy and Potential Determination of the X<sup>1</sup>Σ and the a<sup>3</sup>Σ<sup>+</sup> state of NaCs** — ●M. HOBEIN<sup>1</sup>, A. GERDES<sup>1</sup>, O. DOCENKO<sup>2</sup>, M. TAMANIS<sup>2</sup>, J. ZAHAROVA<sup>2</sup>, R. FERBER<sup>2</sup>, A. PASHOV<sup>3</sup>, H. KNÖCKEL<sup>1</sup>, and E. TIEMANN<sup>1</sup> — <sup>1</sup>Institut für Quantenoptik, Universität Hannover, Welfengarten 1, 30167 Hannover — <sup>2</sup>Department of Physics and Institute of Atomic Physics and Spectroscopy, University of Latvia, Rainis Boulevard 19, LV 1586 Riga, Latvia — <sup>3</sup>Department of Physics, Sofia University, 5 James Bourchier blvd, 1164 Sofia, Bulgaria

With the technique of Fourier-Transform-Spectroscopy of laser-induced fluorescence it is possible to observe fluorescence series due to singlet and triplet transitions simultaneously as long as the excitation is to a mixed singlet-triplet level. The data gained in such type of spectroscopy have been used to derive precise potential energy curves for the ground X<sup>1</sup>Σ state of NaCs [1] and for the a<sup>3</sup>Σ<sup>+</sup> state as well. The PECs allow to derive also the long range scattering properties for cold collisions of Na + Cs, like scattering length and Feshbach resonances.

[1] O. Docenko et al., Eur. Phys. Journal D, **31**, 205, 2004.

MO 57.10 Do 16:30 Labsaal

**Influence of tight traps on photoassociation in ultracold alkali gases** — ●SERGEY GRISHKEVICH and ALEJANDRO SAENZ — AG Moderne Optik, Institut für Physik, Humboldt-Universität zu Berlin, Hausvogteiplatz 5-7, 10117 Berlin

The influence of tight harmonic traps on the photoassociation process in ultracold alkali gases is investigated. As a model system, Li atoms are considered with realistic interatomic interaction potentials. It is demonstrated that the simple rule "tighter trap leads to higher photoassociation rates" as one would expect from a simple spatial-confinement argument is not applicable for all final states. In fact, it is inapplicable for those states with the highest photoassociation rate in the trap-free case. This is in agreement with a general sum rule that can be derived and shows that the sum of the rates to all final states is in fact (almost) independent of the tightness of the trap. The findings for Li atoms are generalized by considering different atomic species as well as artificially modified scattering lengths (as may be implemented by Feshbach resonances). Furthermore, the validity of the usually adopted pseudo-potential approximation (substituting the correct interatomic potential) for describing photoassociation is discussed.

MO 57.11 Do 16:30 Labsaal

**Cryogenic source for cold polar molecules** — ●LAURENS D. VAN BUUREN, PEPIJN W.H. PINKSE, and GERHARD REMPE — Max-Planck-Institut für Quantenoptik, Hans-Kopfermann-Str. 1, 85748 Garching, Germany

Presently, there is a wide interest in cold polar molecules [1]. Dense samples of these molecules allow the study of collisions and chemistry at low temperatures. Such studies are useful in itself, but will also give insight into the possibility of evaporative cooling of these samples. This could lead to a regime where the anisotropic dipole-dipole interaction becomes relatively strong and new phenomena are to be expected. Besides

this, cold polar molecules can be employed in high precision measurements and are candidates for implementation of a quantum computation.

In our group, translational cold molecules ( $T \sim 1$  K) are filtered out of an effusive molecular beam ( $T \sim 160$  K for ammonia) using an electrical guide. The guided molecules have been stored in a trap for 130 ms at a density of  $10^8$  cm $^{-3}$  [2]. These molecules occupy many internal (rovibrational) states. Our first goal is to increase the density of translational

and internally cold molecules by pre-cooling them in a cryogenic helium buffer gas. First measurements of buffer-gas cooled beams show the potential of this technique [3]. Here, the proposed cryogenic source to load cold polar molecules into the electric guide will be presented.

[1] J. Doyle et al., *Eur. Phys. J. D* **31**, 149-164 (2004).

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

[3] S. Maxwell et al., arXiv/physics 0508100 (2005).

## MO 58 Poster: Spectroscopy in He-Droplets

Zeit: Donnerstag 16:30–18:30

Raum: Labsaal

MO 58.1 Do 16:30 Labsaal

**Bildung und Spektroskopie kleiner Alkali-Cluster auf Helium-Nanotröpfchen** — •OLIVER BÜNERMANN und FRANK STIENKEMEIER — Physikalisches Institut, Universität Freiburg, Hermann Herder Str. 3, D-79104 Freiburg

Die Untersuchung von kleinen Clustern gibt darüber Aufschluß, ab welcher Teilchenzahl Festkörpereigenschaften zum Vorschein kommen und zum Beispiel kollektive Anregungen beobachtet werden können. Insbesondere Cluster aus Alkaliatomen sind ausgiebig untersucht worden. Es zeigte sich, dass in diesem Zusammenhang nicht nur die Teilchenanzahl, sondern auch die Temperatur eine entscheidende Rolle spielt[1]. In Helium-Nanotröpfchen können Cluster aus den verschiedensten Materialien gebildet und durch evaporatives Kühlen auf eine Temperatur von 380 mK stabilisiert werden. Somit liefern sie eine ideale Matrix zur Untersuchung von kleinen Clustern bei sehr tiefen Temperaturen.

Wir haben sowohl Cluster aus Natrium als auch Kalium auf Helium-Nanotröpfchen gebildet und mit Hilfe von resonanter zwei Photonen Ionisation untersucht. Es konnten Cluster bis zu Größen von über 50 Atomen auf Helium-Nanotröpfchen nachgewiesen werden. Verschiedene resonante Absorptionen von Kalium-Clustern wurden gefunden, die unterschiedlichen Clustergrößen zugeordnet werden können.

[1] M. Schmidt, C. Ellert, W. Kronmüller, and H. Haberland, Temperature dependence of the optical response of sodium cluster ions  $\text{Na}_n^+$ , with  $4 \leq n \leq 16$ , *Phys. Rev. B* **59**(1999), 10970

MO 58.2 Do 16:30 Labsaal

**Fragmentation von Kaliumclustern isoliert in Helium-Nanotröpfchen** — •P. CLAAS<sup>1</sup>, G. DROPELMANN<sup>1</sup>, C.P. SCHULZ<sup>2</sup>, M. MUDRICH<sup>3</sup> und F. STIENKEMEIER<sup>3</sup> — <sup>1</sup>Fakultät für Physik, Universität Bielefeld — <sup>2</sup>Max-Born-Institut, Berlin — <sup>3</sup>Physikalisches Institut, Universität Freiburg

Die Fragmentation von Kaliumclustern ( $\text{K}_n$ ,  $n = 3 - 11$ ) im Temperaturbereich von Millikelvin lässt sich mit Hilfe von Femtosekunden-Pump-

Probe-Spektroskopie untersuchen. Dazu wurden Helium-Nanotröpfchen mit Kaliumclustern dotiert und Fragmentationszeiten in Abhängigkeit von Photonenenergie, Helium-Tröpfchengröße usw. bestimmt. Interessant hierbei ist der Einfluss der Helium-Umgebung auf die Fragmentation, d.h., die Änderung der Fragmentationszeiten durch die Energieabgabe bzw. Thermalisierung im Helium. Es zeigt sich ein deutlicher Unterschied in den gemessenen Fragmentationszeiten im Vergleich zu Ergebnissen aus Gas-Phasen-Messungen. Die Tröpfchen sind somit in der Lage, Energien im Bereich von 1 eV in weniger als 1 ps aufzunehmen bzw. durch das Abdampfen einzelner Heliumatome abzugeben. Die Ergebnisse geben somit einen direkten Einblick in den Kühlprozess bei der Isolation in Heliumtröpfchen.

MO 58.3 Do 16:30 Labsaal

**Doping Helium nanodroplets by laser ablation / desorption** — •BENJAMIN FORKL<sup>1</sup>, ANDREAS BRANDING<sup>2</sup>, PATRICK CLAAS<sup>2</sup>, FRANK STIENKEMEIER<sup>1</sup>, and MARCEL MUDRICH<sup>1</sup> — <sup>1</sup>Physikalisches Institut, Universität Freiburg — <sup>2</sup>Fakultät für Physik, Universität Bielefeld

Doping He nanodroplets by means of laser ablation of different metals is investigated. Using a Nd:YAG laser at 10 Hz repetition rate, both refractory metals (Ti, Co) as well as alkaline earth atoms (Mg, Ba) are successfully ablated and attached to He nanodroplets. Multiple doping has been observed in the case of Mg and Ba. Furthermore,  $\text{Mg}^+$  and  $\text{Ba}^+$  ion-doped He droplets have been observed at quite different droplet source conditions [1].

A new setup based on a Nd:YLF laser at kHz repetition rate operating at 1054, 527, or 263 nm is presented. Both laser ablation as well as matrix-assisted laser desorption/ionization (MALDI) can be implemented. This new source for doping He droplets is a versatile tool for spectroscopy of neutral and charged atoms up to large molecules at mK temperatures.

[1] P. Claas, S.-O. Mende, and F. Stienkemeier, *Rev. Sci. Instr.* **74** 4071 (2003)

## MO 59 Poster: Experimental Techniques

Zeit: Donnerstag 16:30–18:30

Raum: Labsaal

MO 59.1 Do 16:30 Labsaal

**Ultrathin optical fiber absorption spectroscopy of sub-monolayers at ambient conditions** — •FLORIAN WARREN<sup>1</sup>, E. VETSCH<sup>1</sup>, G. SAGUÉ<sup>1</sup>, D. HAUBRICH<sup>1</sup>, D. MESCHÉDE<sup>1</sup>, M. SOKOLOWSKI<sup>2</sup>, and A. RAUSCHENBEUTEL<sup>1</sup> — <sup>1</sup>Institut für Angewandte Physik, Universität Bonn, Wegelerstr. 8, 53115 Bonn — <sup>2</sup>Institut für Physikalische und Theoretische Chemie, Universität Bonn, Wegelerstr. 12, 53115 Bonn

Ultrathin tapered optical fibers provide strong evanescent fields over almost unlimited length. Such fibers promise to even detect very few molecules or single atoms. In our experiment we demonstrate an extremely sensitive, simple and fast method for absorption spectroscopy of different organic molecules adsorbed at the surface of a fiber at ambient conditions. Furthermore, we are able to resolve the dynamics of agglomerating molecules while undergoing phase transition from gas to adsorbate. This results in a shift and broadening of the absorption spectrum. We discuss the potential for detection of single molecules. Furthermore the investigation of spectra in the strong coupling regime with a micro-cavity such as bottle or Fabry-Perot resonator is considered.

Financial support by the DFG research unit 557 is gratefully acknowledged.

MO 59.2 Do 16:30 Labsaal

**Alternate Gradient Focusing and Deceleration of large molecules** — •JOCHEN KÜPPER, KIRSTIN WOHLFART, FRANK FILSINGER, HENDRICK L. BETHLEM, HENRIK HAAK, and GERARD MEIJER — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin

Over the last years fascinating progress has been made in the spectroscopy of large molecules, e. g. the *building blocks of life* [1]. Such studies allow a detailed understanding of the intrinsic physical and chemical properties of large, modular molecules. The preparation of cold, isolated samples of large molecules and the manipulation of their external degrees of freedom allow further investigations using high-resolution spectroscopy or scattering experiments. Our group has been developing methods to decelerate and store neutral molecules using switched electric fields [2]. Here we show how these techniques can be applied to large molecules, i. e. molecules of biological relevance, for which all low-lying states are practically high-field seeking. Using a novel, modular experiment for the Alternate Gradient deceleration and trapping of molecules in high-field seeking states metastable CO and benzonitrile ( $\text{C}_7\text{H}_5\text{N}$ ) have been decelerated. The results of these experiments are compared to simulations and further experiments on the manipulation of the external degrees of freedom of benzonitrile and large, modular molecules are discussed.

[1] Special issue "Biomolecules in the gasphase" *Eur. Phys. J. D* **20**(3), 309-626 (2002); Special issue "Bioactive molecules in the gasphase" *Phys. Chem. Chem. Phys.* **6**(10), 2543-2890 (2004)

[2] H.L. Bethlem und G. Meijer, *Int. Rev. Phys. Chem.* **22**, 73–128 (2003)

MO 59.3 Do 16:30 Labsaal

**Highly sensitive absorption contrast imaging with a near-field infrared nanoscope** — •ILONA KOPF, GÖTZ WOLLNY, JEAN-SEBASTIEN SAMSON, ERIK BRÜNDERMANN, and MARTINA HAVENITH — Physikalische Chemie II, Ruhr-Universität Bochum

A challenging scientific task is the label-free and non-invasive investigation of molecules with a nanometer scale resolution. Due to the significant absorption lines in the infrared region, the so-called fingerprint region, the

combination of sophisticated apertureless near-field scanning optical microscopy with unique infrared laser spectroscopy is a powerful method to revolutionize our understanding of the chemistry of biomembranes and surfaces. Using microcontact printing we could show that a near-field scanning infrared microscope offers a high sensitivity to chemically resolve molecular monolayers: a longstanding goal in SPM. To deepen the understanding of the chemistry of supported biomembranes additional measurements were performed on liposomes and artificial lipid bilayers with a subwavelength resolution of about 20 nm.

## MO 60 Poster: Various Topics

Zeit: Donnerstag 16:30–18:30

Raum: Labsaal

MO 60.1 Do 16:30 Labsaal

**Beobachtung eines reversiblen Phasenübergangs in dünnen VO<sub>2</sub> - Schichten im fernen Infrarot** — •A. THOMAN<sup>1</sup>, B.M. FISCHER<sup>1</sup>, P. UHD JEPSEN<sup>2</sup>, R. HAGLUND<sup>3</sup> und H. HELM<sup>1</sup> — <sup>1</sup>Freiburger Materialforschungszentrum FMF, Stefan-Meier-Straße 21, 79104 Freiburg — <sup>2</sup>COM.DTU - Department of Communications, Optics, and Materials, DK-2800 Kgs. Lyngby — <sup>3</sup>Vanderbilt Uni, USA

Der Übergang vom Nichtleiter zum Metall (NM) in Vanadiumdioxid (VO<sub>2</sub>) bei Erhöhung der Temperatur ist schon lange bekannt und wurde sehr detailliert untersucht. Trotzdem herrscht noch keine Einigkeit über die Natur des Phasenübergangs. Untersuchungen im mittleren IR [1] deuten auf ein Modell hin, das auf dem Wachstum von metallischen Bereichen basiert, während andere Untersuchungen [2] den homogenen Anstieg der Ladungsträgerkonzentration für die Änderung der Eigenschaften während des Phasenübergangs verantwortlich machen. Wir haben mit Hilfe der Terahertz Time-Domain Spectroscopy (THz-TDS) die optischen Eigenschaften dünner VO<sub>2</sub> Schichten in der Nähe des NM Übergangs im Bereich von 100 GHz - 2 THz untersucht. Es zeigt sich, dass die Fähigkeit der THz-TDS, sowohl die Amplitude als auch die Phase der Transmission zu messen, entscheidend bei der Interpretation der Ergebnisse ist. Die temperaturabhängige Amplitude ergab eine deutlich andere Schalttemperatur als die Phase. Dieser Effekt wurde nach unserem Wissen bisher noch nicht beobachtet und ist sehr wichtig für die Deutung der Ergebnisse. Unsere Daten zeigen eine sehr gute Übereinstimmung mit dem domain growth Modell. [1] H.S.Choi et al, *Phys. Rev. B* 54, 4621 (1996), [2] A. Zylbersztejn and N.F. Mott, *Phys.Rev. B* 11, 4383 (1975)

MO 60.2 Do 16:30 Labsaal

**Elektronendichroismus** — •ANDRÉ H. ZIMNOL und G. FRIEDRICH HANNE — Westfälische Wilhelms-Universität Münster, Physikalisches Institut, Wilhelm-Klemm-Str. 10, 48149 Münster

Die unterschiedliche Abschwächung longitudinal spinpolarisierter Elektronen nach Transmission durch in der Gasphase vorliegende chirale Moleküle wird als Elektronendichroismus bezeichnet. Theoretische Rechnungen mit einfachen Modellmolekülen sagen eine Transmissionsasymmetrie in der Größenordnung  $1 \cdot 10^{-4}$  voraus, wobei in den Modellen die Spin-Bahn-Wechselwirkung als Ursache angenommen wird. Untersuchungen von Mayer, Nolting und Kessler [1] bestätigen den Effekt, die leichte Substanz Kampfer C<sub>10</sub>H<sub>16</sub>O weist im Gegensatz zu der bromierten Form praktisch keinen Elektronendichroismus auf. Messungen an Verbindungen mit Atomen zunehmender Ordnungszahl zeigen allerdings nicht den erwarteten Anstieg im Asymmetriesignal, wie es aufgrund der Wechselwirkung zu erwarten ist. Für eine genauere Analyse des Elektronendichroismus ist die verwendete Apparatur bezüglich der Nachweisgrenze optimiert worden. Kampfer sowie andere leichte Verbindungen, unter anderem Alkohole, werden hinsichtlich einer Transmissionsasymmetrie untersucht.

[1] S Mayer, C Nolting and J Kessler, *Electron scattering from chiral molecules*, *J. Phys. B: At. Mol. Opt. Phys.* 29 (1996) pp 3497-3511

## MO 71 Dynamics and Spectroscopy at Interfaces

Zeit: Freitag 10:40–12:25

Raum: H12

MO 71.1 Fr 10:40 H12

**Ultrafast heterogeneous electron transfer: escape dynamics of injected electrons** — •LARS GUNDLACH, RALPH ERNSTORFER, JODI SZARKO, ANTJE NEUBAUER, LIANA SOCACIU-SIEBERT, and FRANK WILLIG — Hahn-Meitner-Institute, Department: Dynamics of Interfacial Reactions SE4, Glienickestrasse 100, 14109 Berlin, Germany

So far, most investigations of heterogeneous electron transfer focused on the time scale the electrons take to leave the molecules. Here, we report on the dynamics taking place after the electron has left the molecule. Ultrafast electron escape dynamics following excitation of the interfacial charge transfer complex of catechol prepared on the rutile TiO<sub>2</sub>(110) surface was investigated with femtosecond two-photon photoemission.

Photo-induced interfacial charge transfer was instantaneous. Thus, the rise of the signal was controlled by the crosscorrelation function. The energy distribution of the hot electrons generated at the surface was measured as 2PPE spectra. The decay of the 2PPE signal was non-exponential with time constants ranging from 10 fs to picoseconds. It was attributed to the release of the electrons from the surface and escape into the bulk of the semiconductor.

MO 71.2 Fr 10:55 H12

**Structural influence of the dye on the dynamics of ultrafast heterogeneous electron transfer in a dye/semiconductor system** — •ANTJE NEUBAUER, LARS GUNDLACH, LIANA SOCACIU-SIEBERT, JODI SZARKO, RALPH ERNSTORFER, SILKE FELBER, GUIDO MORBACH, RAINER EICHBERGER, and FRANK WILLIG — Hahn-Meitner-Institute, Dept. SE4, Glienicke Str. 100, 14109 Berlin, Germany

The organic dye perylene attached via different anchor and spacer

groups to TiO<sub>2</sub> surfaces were investigated in order to elucidate the influence of the molecular structure of the dye molecules on the dynamics of ultrafast heterogeneous electron transfer. For the electron transfer, the perylene functions as the electron donor in which the donor state lies above the edge of the conduction band minimum of the acceptor TiO<sub>2</sub>. The electron transfer to TiO<sub>2</sub> surfaces has significant importance in the Graetzel cell, a dye-sensitized solar cell. The investigations were performed with two different time-resolved methods. Measurements with two photon photoemission (2PPE) spectroscopy were carried out on a rutile TiO<sub>2</sub> (110) single crystal surface and measurements with transient absorption were done on colloidal films of anatase TiO<sub>2</sub>. Both techniques were employed under UHV conditions to avoid the photodecomposition of the perylene chromophore in the presence of water. The results of both methods on different perylene-derivatives at the TiO<sub>2</sub> surfaces will be shown and compared.

MO 71.3 Fr 11:10 H12

**Observation of pH dependent back-electron transfer dynamics in Alizarin - TiO<sub>2</sub> adsorbates: Importance of trap states** — •MATYLITSKY VICTOR, LENZ MARTIN, and WACHTVEITL JOSEF — Goethe -University Frankfurt/Main, Institute of Physical and Theoretical Chemistry, Marie-Curie-Str. 11, D-60439 Frankfurt/Main, Germany

The dependence of the interfacial electron transfer in alizarin sensitized TiO<sub>2</sub> nanoparticles from sample pH has been examined via transient absorbance spectroscopy in the visible spectral region. Excitation of the alizarin/TiO<sub>2</sub> system leads to a very fast electron injection (<100 fs) over a wide pH range. Back electron transfer shows a complicated multiphasic kinetics and strongly depends on the acidity of the solution. The

drastic changes in electron transfer dynamics upon varying the pH are explained by Nernstian-type change in the semiconductor band energy. Indeed, a change of sample pH values over seven units leads to a  $\sim 0.42$  eV change of the conduction band edge position (i.e. the nominal free energy of the electron in the electrode). This change was sufficient to push the system to a condition, where direct electron injection to intraband gap surface states could be investigated. The existence of an electron transfer pathway via surface trap states is supported by the similarity of the observed back electron transfer kinetics of alizarin/TiO<sub>2</sub> at pH 9 and alizarin/ZrO<sub>2</sub> reported in earlier work (J. Phys. Chem. B 2000, 104, 8995), where the conduction band edge is approximately 1eV above the excited state of the dye. The influence of surface trap states on interfacial electron transfer and a detailed analysis of their population, depopulation and relaxation kinetics will be presented.

MO 71.4 Fr 11:25 H12

**Influence of the Organic Cappings of CdSe Nanoparticles on the Charge Carrier Relaxation Dynamics** — •TOBIAS E. SCHRADER<sup>1</sup>, BIRGIT VON HOLT<sup>1</sup>, STEPHAN MALKMUS<sup>1</sup>, THOMAS BRUST<sup>1</sup>, WOLFGANG J. SCHREIER<sup>1</sup>, FLORIAN O. KOLLER<sup>1</sup>, STEFAN KUDERA<sup>2</sup>, WOLFGANG PARAK<sup>2</sup>, and MARKUS BRAUN<sup>1</sup> — <sup>1</sup>Ludwig-Maximilians-Universität, Lehrstuhl für BioMolekulare Optik, Oettingenstr. 67, 80538 München — <sup>2</sup>Ludwig-Maximilians-Universität, Lehrstuhl für Angewandte Physik, Amalienstr. 54, 80799 München

CdSe nanoparticles (NPs) have attracted much scientific interest because of their potential applications in labelling proteins in living cells. Organic cappings of NPs serve two purposes: Firstly they determine the surface chemistry of the NPs and therefore are a key to biological applications. Secondly they improve the fluorescence quantum yield which is crucial for the application as protein markers. With time resolved visible pump, visible and infrared probe spectroscopy we have investigated the charge carrier dynamics in NPs. With the electron acceptor naphthoquinone as capping faster decay times (90 ps and 1.3 ns) of the  $1\ S_{3/2}$  to  $1\ S_e$  transition at 4.6  $\mu\text{m}$  are observed as compared for the hole acceptor pyridine (120 ps and 4.1 ns). This can be interpreted by the fact that naphthoquinone provides efficient traps to the electron whose signal is observed in the IR transient.

MO 71.5 Fr 11:40 H12

**Molecular view of hidden interfaces** — •SYLVIE ROKE — Max-Planck Institute for Metals Research, Heisenbergstr. 3, 70569 Stuttgart

Many important chemical, physical and biological phenomena occur at interfaces of small particles. Most of the tools presently available to study these interfaces use invasive techniques or model systems. Ideally, one would want a non-invasive technique that allows the study of interface structure and dynamics with molecular specificity.

By combining light scattering and femtosecond vibrational sum frequency generation (a technique that has been used to mostly study flat interfaces) we are able to study the interfaces of sub-micron particles in solution on a molecular level. Using a nonlinear Rayleigh Gans Debye model we can extract information about the order and orientation of interface molecules and simultaneously obtain the shape and size of the particles [1]. Two demonstrations of sum frequency scattering will be presented. The first will deal with colloidal dispersions of sterically stabilized silica particles that undergo a gelation transition [2].

Second, we will present valuable insights in the interface properties of lactate particles, which are being used as a new medicine against liver

malignancies [3].

[1] S. Roke, et al. Phys. Rev. Lett., 91, 258302 (2003).

[2] S. Roke et al. to be published in J. Phys: Condens Matter., 17, S3467 (2005)

[3] J. F. W. Nijsen et al., Eur. J. Nucl. Med. B, 26, 699 (1999)

MO 71.6 Fr 11:55 H12

**Surface Enhanced Raman Spectroscopy (SERS) with Nano-Structured Gold Surfaces** — •M. SACKMANN, T. BALSTER, and A. MATERNY — International University Bremen, Bremen

Raman spectroscopy is a common tool for qualitative and quantitative chemical analysis of molecules even in a mixture of different substances. Although, the unique identification of adenine molecules is possible via their vibrational lines, high concentrations (mmol/l) are needed for qualitative results due to the low scattering cross section for non-resonant excitation. The intensity of the Raman spectra is amplified by the use of the Surface Enhanced Raman Scattering (SERS) technique. While the use of silver sols only results in a limited reproducibility of the Raman line intensities, nano-structured gold surfaces, if used as SERS-active substrates, in principle should combine the high sensitivity with better reproducibility. For this purpose, we have produced gratings of gold dots on Si(001) surfaces by means of electron beam lithography. The distance between the gold nanostructures was varied between 350 to 370 nm and for the diameters of the gold dots values between 50 to 320 nm were chosen. The samples are characterized by reflection spectroscopy, to determine the resonance of the grating structure. Recent measurement results with Raman microscopy of adenine (ppm concentrations) on these structures will be presented.

MO 71.7 Fr 12:10 H12

**Extreme Adsorption Capability of Nanodiamond and Detectability of Lysozyme Concentration by Fluorescence Method** — •VICTOR WEI-KEH WU<sup>1,2,3</sup> and KOWA CHEN<sup>1</sup> —

<sup>1</sup>Inst. of Atomic and Molecular Sci., Academia Sinica, P.O.Box 23-166, 10617 Taipei Taiwan — <sup>2</sup>Dept. of Chem. Eng., National Kaohsiung Univ. of Appl. Sci., 80782 Kaohsiung, Taiwan — <sup>3</sup>Victor Basic Res. Lab. e. V., Gadderbaumer-Str. 22, 33602 Bi., Germany, <http://www.che.kuas.edu.tw>

UV-Absorbance has been applied usually, for resolution of Lysozyme (containing 4 tryptophanes) up to ca. 50-100  $\mu\text{M}$ , via Sore band at 409 nm. The adsorption capability of Nanodiamond (ND)  $\phi=100$  nm - nearly all kinds of proteins in a sol. can be completely adsorbed<sup>1</sup>, and the detectability of extremely diluted lysozyme solution are demonstrated. Diff. conc. of lysozyme (M=14300 g/mole, Sigma Chemical) of chicken egg white betw. 1-500 nM were prepared in KPBS buffer sol. of 7 mM. Xenon Lamp (2500 W, L.P. Associates, Inc.) for 285 nm with 3 mm slit width was used. A quartz cuvette with 10x10 cross section was used. Sol. well stirred, fluorescence was collected perpendicularly with PMA-11 of Hamamatsu. The linearity of the detected fluorescence counts depend upon the lysozyme conc. betw. 10-500 nM was well measurable. The ND used, was 5-20  $\mu\text{g}$ . The lysozyme adsorption capability by ND can be distinguishably followed down to 10 nM. This is  $10^4$  as powerful as by UV-Absorbance, and can be a new method for doping control<sup>2</sup>. \*Wu is the correspondence author. Ref. 1. X.-L. Kong, et al., AC. 77, 259 (2005), 2. J. Wallrafen, GIT, 49, 644 (2005).

## MO 72 Collisions and Energy Transfer

Zeit: Freitag 10:40–12:40

Raum: H10

MO 72.1 Fr 10:40 H10

**Hochauflösende Elektronenanlagerung an SF<sub>6</sub>, SF<sub>5</sub>Cl und SF<sub>5</sub>CF<sub>3</sub>** — •M. BRAUN<sup>1</sup>, C. A. MAYHEW<sup>2</sup>, M.-W. RUF<sup>1</sup> und H. HOTOPI<sup>1</sup> — <sup>1</sup>Fachbereich Physik, TU Kaiserslautern, D-67653 Kaiserslautern, Germany — <sup>2</sup>Schools of Physics and Astronomy and Chemistry, University of Birmingham, Edgbaston, Birmingham, B15 2TT, UK

SF<sub>6</sub>, SF<sub>5</sub>Cl und vor allem SF<sub>5</sub>CF<sub>3</sub> sind starke Treibhausgase, daher ist das Verständnis der Dissoziation durch Stöße langsamer Elektronen mit diesen Molekülen von erheblichem Interesse. Mit der LPA/EXLPA - Methode [1] haben wir daher für diese Moleküle die Anionenbildung bei der Anlagerung von Elektronen im Energiebereich 0 - 2 eV mit

hoher Auflösung untersucht. In allen Fällen wird bei kleinen Energien s-wave Attachment beobachtet, wobei für SF<sub>6</sub> hauptsächlich langlebige SF<sub>6</sub><sup>-</sup> Anionen gebildet werden. Für SF<sub>5</sub>CF<sub>3</sub> entstehen ausschließlich und für SF<sub>5</sub>Cl überwiegend SF<sub>5</sub><sup>-</sup> Anionen, wobei die Querschnitte im Bereich 0.05-0.5 eV um Faktoren 10 bzw. 500 abfallen.

Für SF<sub>6</sub> wird oberhalb von 0.3 eV dominant SF<sub>5</sub><sup>-</sup> gebildet mit einem Maximum bei 0.56 eV. Erstmals wurden an den Schwellen für Schwingungsanregung der  $\nu_1$ -Mode in der SF<sub>5</sub><sup>-</sup> Produktion bis zu  $\nu_1 = 10$  Wignersche Cusp-Strukturen gefunden, die darauf hindeuten, dass die Erzeugung von SF<sub>6</sub><sup>-</sup> und SF<sub>5</sub><sup>-</sup> über einen gemeinsamen SF<sub>6</sub><sup>-</sup> - Streuzustand erfolgt [2]. Diese Arbeit wurde unterstützt durch die DFG und den FSP OTLAP.

[1] M. Braun, S. Barsotti, S. Marienfeld, E. Leber, J. M. Weber, M.-W.

Ruf, H. Hotop, Eur. Phys. J. D **35** (2005) 177

[2] M. Braun, M.-W. Ruf, H. Hotop, and M. Allan, Chem. Phys. Lett. (in press)

MO 72.2 Fr 10:55 H10

**Anlagerung langsamer Elektronen an selektiv schwingungsangeregte SF<sub>6</sub> Moleküle** — ●M. BRAUN<sup>1</sup>, F. GRUBER<sup>1</sup>, E. ILLENBERGER<sup>2</sup>, S.V.K. KUMAR<sup>3</sup>, M.-W. RUF<sup>1</sup> und H. HOTOP<sup>1</sup> — <sup>1</sup>Fachbereich Physik, TU Kaiserslautern, D-67653 Kaiserslautern, Germany — <sup>2</sup>Fachbereich Chemie, FU Berlin, D - 14195 Berlin, Germany — <sup>3</sup>Tata Institute of Fundamental Research, Mumbai 400 005, India

Die Anlagerung freier Elektronen an SF<sub>6</sub> - Moleküle unter Bildung langlebiger SF<sub>6</sub><sup>-</sup> - Ionen ist ein wichtiger Prozess in gasförmigen Dielektrika [1]. Während das Verhalten des Querschnitts unterhalb von 0.1 eV gut verstanden ist, sind hinsichtlich der Bildung von SF<sub>6</sub><sup>-</sup> Ionen noch Fragen offen: Verläuft letztere über eine repulsive Resonanz bei etwa 0.5 eV oder ist sie Resultat eines partiellen Zerfalls des SF<sub>6</sub><sup>-</sup> Komplexes? Welchen genauen Einfluss haben Elektronenenergie und rovibronische Energie des Ausgangsmoleküls auf die Dissoziation dieses Komplexes? Zur Klärung haben wir mittels der LPA/EXLPA Methode hochauflösende Messungen der Querschnitte für die Bildung von SF<sub>6</sub><sup>-</sup> und SF<sub>5</sub><sup>-</sup> Ionen im Energiebereich 0 - 2 eV mit einem geseedeter Düsenstrahl (Temperaturen 300 - 600 K) durchgeführt. Zur Anregung der Moleküle wurde transversal ein CO<sub>2</sub> - Laser (Leistung bis 60 W, Strahldurchmesser etwa 2 mm) eingestrahlt und mit mehreren Linien gezielt die  $\nu_3$  Schwingungsmoden gepumpt. Die CO<sub>2</sub> Laseranregung führt zu einer von der Elektronenenergie abhängigen Erhöhung der SF<sub>5</sub><sup>-</sup> Bildung um bis zu 80%.

Diese Arbeit wurde unterstützt durch die DFG und den FSP OTLAP.

[1] L. G. Christophorou, J. K. Olthoff, J. Phys. Chem. Ref. Data **29** (2000) 267

MO 72.3 Fr 11:10 H10

**Untersuchung der Winkelabhängigkeit der Dissoziativen Rekombination von CH<sup>+</sup> und HD<sup>+</sup>** — ●S. NOVOTNY<sup>1</sup>, H. RUBINSTEIN<sup>2</sup>, V. ANDRIANARJAONA<sup>1</sup>, H. BUHR<sup>1</sup>, J. HOFFMANN<sup>1</sup>, L. LAMMICH<sup>1</sup>, M. LESTINSKY<sup>1</sup>, I. NEVO<sup>2</sup>, D. SHAFIR<sup>2</sup>, D. ZAJFMAN<sup>2</sup>, D. SCHWALM<sup>1</sup> und A. WOLF<sup>1</sup> — <sup>1</sup>Max-Planck Institut für Kernphysik, Heidelberg — <sup>2</sup>Weizmann Institute of Science, Rehovot, Israel

Mit Hilfe eines drei-dimensionalen Detektors [1], der sowohl die Position als auch die Auftreffzeiten neutraler Fragmente messen kann, wurde der Prozess der dissoziativen Rekombination (DR) von CH<sup>+</sup> und HD<sup>+</sup> untersucht. In diesem Prozess werden durch Elektroneneinfang über einen hochangeregten Molekülzustand neutrale Fragmente mit möglicher kinetischer Energie gebildet. Unter Annahme einer langsamen Rotation des Molekülions verglichen zur Zeitskala des DR Prozesses, lässt sich direkt aus der Winkelverteilung der entstehenden Fragmente auf die Abhängigkeit der DR Reaktion von dem Winkel zwischen Elektron und Molekülachse schließen. In unseren Messungen wurde die Abhängigkeit der Winkelverteilungen für verschiedene Einfallenergien der Elektronen an CH<sup>+</sup>[2] und HD<sup>+</sup> untersucht. Die Sensitivität der Messung verlangt es, dass die Eigenschaften des Elektronenstrahls, d.h. die longitudinale und transversale Elektronentemperatur, für eine komplette Beschreibung der Daten mit berücksichtigt werden müssen.

[1] D. Strasser et al., Rev. Sci. Instrum. **71**, 3092 (2000)

[2] S.L. Guberman, J.P.Conf. Ser. **4**, 58 (2005)

MO 72.4 Fr 11:25 H10

**Crossed beam study of the charge transfer from Ar<sup>+</sup> to N<sub>2</sub>** — ●J. MIKOSCH<sup>1,2</sup>, S. TRIPPEL<sup>1</sup>, R. BERHANE<sup>1</sup>, R. OTTO<sup>1</sup>, D. SCHWALM<sup>2</sup>, M. WEIDEMÜLLER<sup>1</sup>, and R. WESTER<sup>1</sup> — <sup>1</sup>Physikalisches Institut, Universität Freiburg, 79104 Freiburg — <sup>2</sup>Max-Planck-Institut für Kernphysik, 69117 Heidelberg

Charge transfers are probably the most simple class of chemical reactions. Although chemical bonds are neither broken nor formed, this does surprisingly not impede charge transfer to be remarkably state-selective. In the electron transfer from Ar<sup>+</sup> to N<sub>2</sub>( $v=0$ ) at low collision energies, the product ion N<sub>2</sub><sup>+</sup> is left most likely in the first excited vibrational state via an endothermic channel with  $\Delta E = -92$ meV. This non-adiabatic process is observed despite the fact, that production in the vibrational groundstate N<sub>2</sub><sup>+</sup>( $v=0$ ) is exothermic by 179meV.

We have used this reaction as a benchmark for our new apparatus, which combines crossed beams with velocity map imaging [1] to study reactive collisions at scattering energies below 1eV. For image analysis, a Monte Carlo Reconstruction (MCR) method has been developed. Within a narrow energy window we have observed large angle scattering. Also

higher vibrational states seem to be populated in the N<sub>2</sub><sup>+</sup> product ion, which will be compared to earlier measurements [2]. An outlook on the study of nucleophilic substitution reactions, which are interesting due to their highly non-statistical behaviour, will be given.

[1] A.Eppink & D.Parker, Rev.Sci.Instr. **68**, 3477 (1997) [2] K.Birkinshaw, A.Shukla, S.Howard and J.Futrell, Chem. Phys. **113**, 149 (1987)

MO 72.5 Fr 11:40 H10

**Nicht-adiabatische Kopplungen beim Dreiteilchenzerfall von H<sub>3</sub>: Deutung von Impulskorrelationen mit Hilfe klassischer Trajektorien** — ●ULRICH GALSTER<sup>1</sup>, FRANK BAUMGARTNER<sup>1</sup>, MARTIN JUNGEN<sup>2</sup> und HANSPETER HELM<sup>1</sup> — <sup>1</sup>Physikalisches Institut der Universität Freiburg — <sup>2</sup>Institut für physikalische Chemie, Universität Basel

Nicht-adiabatische Prozesse gehören zu den am wenigsten verstandenen und momentan am intensivsten untersuchten Gebieten der fundamentalen Molekülphysik. Sie sind verantwortlich für Störungen in Absorptions- und Emissionsspektren und haben einen wesentlichen Einfluss auf die Molekülbildung und -dissoziation. Als einfachstes mehratomiges Molekül ist das H<sub>3</sub> ein hervorragend geeignetes Objekt für die experimentelle und theoretische Untersuchung nicht-adiabatischer Prozesse. In diesem Beitrag werden neue, umfangreiche experimentelle Ergebnisse über die Impulskorrelationen beim Dreiteilchenzerfall von zustandsselektierten H<sub>3</sub>-Molekülen präsentiert. Aus der Komplexität der Korrelationsmuster lässt sich mit Hilfe detaillierter Daten von adiabatischen Zustandsflächen auf den jeweiligen Dissoziationspfad schließen [1]. Es wird zudem eine Methode vorgestellt, wie anhand von klassischen Trajektorien Informationen über die geometrische Abhängigkeit nicht-adiabatischer Kopplungen gewonnen werden können.

[1] Galster, Baumgartner, Müller, Helm, Jungen, Phys.Rev.A, **72** (2005) (accepted)

MO 72.6 Fr 11:55 H10

**Untersuchung zur reaktiven Streuung von NH<sub>3</sub><sup>+</sup> an filmbelegten In<sub>2</sub>O<sub>3</sub> : SnO<sub>2</sub> (ITO)-Oberflächen** — ●THOMAS KOLLING und KARL-MICHAEL WEITZEL — Philipps Universität Marburg, Fachbereich Chemie, Physikalische Chemie

In diesem Beitrag werden experimentelle Ergebnisse zur Untersuchung von Ionen-Oberflächenreaktionen mit zustandsselektierten Molekülionen vorgestellt. Hierbei werden zustandsselektierte NH<sub>3</sub><sup>+</sup>-Molekülionen durch resonanzverstärkte Multiphotonenionisation (REMPI) in einer Ionenquelle erzeugt. Die Ionen werden anschließend durch ein elektrostatisches Linsensystem in die Streukammer geführt, wo die Wechselwirkung mit einer Oberfläche als Funktion der kinetischen Energie und des Quantenzustandes untersucht werden kann. Die Reaktionsprodukte werden anschließend mit einem Flugzeitmassenspektrometer analysiert. Charakteristische Kennwerte des Experimentes werden dargestellt. Hier wurde die reaktive Streuung von NH<sub>3</sub><sup>+</sup>-Ionen an einer mit einem NH<sub>3</sub>-Film belegten ITO-Oberfläche als Funktion der kinetischen Energie untersucht. Bei kleinen Stoßenergien wird die Aufnahme von H-Atomen aus dem Film unter NH<sub>4</sub><sup>+</sup>-Bildung beobachtet. Bei höheren Stoßenergien wird die H-Abspaltung aus NH<sub>3</sub><sup>+</sup> beobachtet. Diese Zuordnung soll anhand von Deuterium markierten Experimenten überprüft werden.

MO 72.7 Fr 12:10 H10

**Dispersive Delocalization Length on J-Aggregates from Nonlinear Absorption** — ●CHRISTIAN SPITZ<sup>1</sup>, HERBERT LEGALL<sup>2</sup>, HOLGER STIEL<sup>2</sup>, and RALF MENZEL<sup>1</sup> — <sup>1</sup>Universität Potsdam — <sup>2</sup>MBI-Berlin

Excitons in two-dimensional molecular aggregates of TDBC were investigated by nonlinear absorption and pump-probe spectroscopy in ps resolution. It is shown how the delocalization length of the optical excitation can be determined by these measurements.

The main result obtained by this experiments is a dispersive delocalization length of the excitons. This can be interpreted, within exciton theory, as excitation of levels with equal eigenvalues but with different degree of delocalization, and therefore different energies. This assumption was proofed by modeling the absorption spectrum, based on dispersive coherence length, which fits well to the experimental results.

MO 72.8 Fr 12:25 H10

**Höchstempfindliche Absorptionsmessungen der Niederdruckflamme im Resonator eines Er-dotierten Faserlasers —**

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Das Emissionsspektrum eines Er-dotierten Faser-Lasers, der durch einen Dioden-Laser bei 980 nm gepumpt wird, verändert sich sehr empfindlich durch spektral selektive Verluste im Laser-Resonator. Dies ermöglicht höchstempfindliche Messungen der Absorption von Gasen im

Resonator. Die Laseremission kann von 1,53  $\mu\text{m}$  bis 1,61  $\mu\text{m}$  durchgestimmt werden. Die Empfindlichkeit der Absorptionsmessungen entspricht einer äquivalenten Absorptionslänge von mehr als 30 km. Mit diesem Laser wurden die Spektren von  $\text{C}_2\text{H}_2$  bei verschiedenen Konzentrationen aufgenommen und identifiziert. Außerdem wurden erstmals die Absorptionsspektren einer Niederdruckflamme von  $\text{CH}_4 + \text{O}_2 + \text{CH}_4 + \text{NH}_3$  als Funktion des Abstands zum Brenner mit hoher Empfindlichkeit aufgenommen. Aus den Spektren wurde die Veränderung der Konzentrationen von  $\text{NH}_3$  und dem Zwischenprodukt  $\text{HCN}$  als Funktion der Entfernung zum Brenner gemessen. Die Messungen können zur Optimierung von Verbrennungsprozessen eingesetzt werden.