Fachverband Molekülphysik (MO)

Eberhard Riedle
Lehrstuhl für BioMolekulare Optik
Department für Physik - LMU München
Oettingenstrasse 67
80538 München
eberhard.riedle@physik.uni-muenchen.de

Symposium SYMC

Der Fachverband veranstaltet zusammen mit dem Fachverband Quantenoptik und Photonik das Symposium „Molecular Collisions at ultracold temperatures“. Das Symposium SYMC findet am Montag, 14:00-16:00 und 16:30-18:30 im Hörsaal 5D statt. Details zum Programm finden Sie im Bereich SYMC.

Symposium SYFM

Der Fachverband veranstaltet zusammen mit dem Fachverband Quantenoptik und Photonik das Symposium „Quantenkontrolle funktionaler Moleküle“. Das Symposium SYFM findet am Mittwoch, 14:00-16:00 und 16:30-18:30 im Hörsaal 6C statt. Details zum Programm finden Sie im Bereich SYFM.

Symposium SYSX

Der Fachverband veranstaltet zusammen mit dem Fachverband Atomphysik das Symposium „Soft X-ray induced ultrafast processes on the atomic scale“. Das Symposium SYSX findet am Donnerstag, 14:00-16:00 und 16:30-17:30 im Hörsaal 6G statt. Details zum Programm finden Sie im Bereich SYSX.

Übersicht der Hauptvorträge und Fachsitzungen

(Hörsäle 5M, 6B, 6C, 6D, 6F und 6J; Poster A)

Haupt- und Preisträgervorträge

MO 22.1	Di	10:30–11:00	6B	**Ultracold Molecular Ions in Radiofrequency Traps - Production and Spectroscopy** — •Bernhard Roth, Jeroen Koelemeij, Chaobo Zhang, David Offenberg, Andreas Wicht, Ingo Ernsting, Stephan Schiller
MO 23.1	Di	14:00–14:30	6C	**Bewegte Bilder auf atomarer Längen- und Zeitskala: Femtosekunden Röntgenbeugung** — •Matias Bargheer
MO 25.1	Di	14:00–14:30	6B	**Manipulating large molecules: selecting isomers, orienting, and slowing polar molecules with strong electric fields** — •Jochen Küpper

Fachsitzungen

MO 11.1–11.8	Mo	14:00–16:00	6B	**Biomolecules**
MO 12.1–12.5	Mo	14:00–15:15	6D	**Femtosecond Spectroscopy I**
MO 13.1–13.9	Mo	16:30–18:45	6B	**Photochemistry**
MO 14.1–14.6	Mo	16:30–18:00	6D	**Molecular Clusters**
MO 21.1–21.7	Di	10:30–12:30	6D	**Femtosecond Spectroscopy II**
MO 22.1–22.8	Di	10:30–12:45	6B	**Cold Molecules I (gemeinsam mit Q)**
MO 23.1–23.1	Di	14:00–14:30	6C	**Gustav-Hertz-Preis (Preisträgervortrag, gemeinsam mit K)**
MO 24.1–24.7	Di	14:30–16:15	6C	**Femtosecond Spectroscopy III**
MO 25.1–25.8	Di	14:00–16:15	6B	**Cold Molecules II (gemeinsam mit Q)**
MO 26.1–26.4	Di	16:30–18:30	Poster A	**Poster: Biomolecules**

MO 27.1–27.3	Di	16:30–18:30	Poster A	**Poster: Collisions and Energy Transfer**
MO 28.1–28.1	Di	16:30–18:30	Poster A	**Poster: Cluster**
MO 29.1–29.12	Di	16:30–18:30	Poster A	**Poster: Cold Molecules**
MO 30.1–30.5	Di	16:30–18:30	Poster A	**Poster: Spectroscopy in He droplets**
MO 31.1–31.2	Di	16:30–18:30	Poster A	**Poster: Quantum Chemistry (Theory)**
MO 41.1–41.4	Mi	11:30–12:30	6B	**Electronic and Radiofrequency Spectroscopy**
MO 42.1–42.3	Mi	11:30–12:15	6D	**Quantum Chemistry (Theory)**
MO 51	Do	11:30–12:30	6D	**Mitgliederversammlung des Fachverbands Molekülphysik**
MO 52.1–52.7	Do	14:00–15:45	6B	**Femtosecond Spectroscopy IV**
MO 53.1–53.6	Do	14:00–15:45	6D	**New Experimental Techniques**
MO 54.1–54.2	Do	16:30–18:30	Poster A	**Poster: Electronic Spectroscopy**
MO 55.1–55.2	Do	16:30–18:30	Poster A	**Poster: Photochemistry**
MO 56.1–56.15	Do	16:30–18:30	Poster A	**Poster: Femtosecond Spectroscopy**
MO 57.1–57.6	Do	16:30–18:30	Poster A	**Poster: Quantum Control**
MO 58.1–58.2	Do	16:30–18:30	Poster A	**Poster: Molecular Dynamics (Theory)**
MO 59.1–59.3	Do	16:30–18:30	Poster A	**Poster: Experimental Techniques**
MO 61.1–61.8	Fr	10:30–12:30	6F	**Quantum Control I**
MO 62.1–62.6	Fr	10:30–12:15	5M	**Collisions with electrons and ions (gemeinsam mit A)**
MO 63.1–63.8	Fr	10:30–12:45	6B	**Spectroscopy in He-droplets / Ultracold Molecules I (gemeinsam mit Q)**
MO 64.1–64.8	Fr	14:00–16:00	6F	**Quantum Control II**
MO 65.1–65.6	Fr	14:00–15:45	6J	**Ultracold Molecules II (gemeinsam mit Q)**

Mitgliederversammlung des Fachverbands Molekülphysik

Donnerstag 11:30–12:30 Hörsaal 6D

- Bericht aus dem Vorstandsrat und zur Entwicklung des Fachverbands
- Bestätigung von Karl Kleinermanns (neuer Leiter des Fachverbands) und Wahl des stellvertretenden Leiters
- Planung der nächsten Tagungen
- Zukünftige Aktivitäten des Fachverbands
- Sonstiges, Wünsche und Anregungen

MO 11: Biomolecules

Zeit: Montag 14:00–16:00 Raum: 6B

MO 11.1 Mo 14:00 6B

IR/UV-double resonance spectroscopy of electronically excited flavonoids — •Kristina Bartl[1], Holger Fricke[1], Kirsten Schwing[1,2], Andreas Funk[1], and Markus Gerhards[1,2] — [1]H.-Heine Universität Düsseldorf, Institut für Physikalische Chemie I, 40225 Düsseldorf — [2]TU Kaiserslautern, Fachbereich Chemie, 67663 Kaiserslautern

Flavonoids are well known for their antioxidative effect. Spectroscopically, flavonoids like 3-hydroxyflavone or 5-hydroxyflavone are of special interest, since a keto-enol-tautomerism takes place after electronic excitation. In order to obtain detailed structural information on the reaction coordinate, combined IR/UV-spectroscopy is applied on electronically excited states in a mass selective molecular beam experiment: In a first step an isomer selective resonant excitation in different electronically excited states is performed and the IR-spectra of these excited states are analyzed by resonant IR-excitation followed by UV-ionisation. By comparison with the isomer selective IR-spectra of the ground state (obtained by another combined IR/UV method) and in combination with ab initio and DFT calculations, structural changes can be identified in detail. Not only the structure sensitive coordinates of the OH and C=O stretching vibrations but also the whole IR spectrum up to the upper fingerprint region can be analyzed by using a newly developed IR laser system. In this presentation investigations of different hydroxyflavones, starting with 3-hydroxyflavone and its clusters with water are presented. Different isomers as well as reaction coordinates are discussed.

MO 11.2 Mo 14:15 6B

The Photophysics of 10-Methylisoalloxazine: A Quantum Chemical Investigation — •Susanne Salzmann and Christel Marian — Institute of Theoretical Chemistry and SFB663, Heinrich Heine Universität Düsseldorf, Universitätsstr. 1, 40225 Düsseldorf, Germany

In recent years flavins have recieved growing attention due to their decisive role as cofactors in phototropins. In the LOV (light, oxygen, and voltage sensitive) domain of the blue light receptor the primary step after light absorption involves a rapid decay of the excited singlet state to the lowest excited triplet state via an intersystem crossing (ISC) mechanism. In aqueous solution, the free flavin shows a different behaviour, the ISC efficiency decreases and the fluorescence increases in comparison to the LOV domain.

Vertical and adiabatic electronic spectra of 10-methylisoalloxazine have been investigated by means of combined density functional and multi-reference configuration interaction methods. Spectral shifts due to electrostatic interactions in aqueous solution are taken into account employing the conductor-like screening model. Spin-orbit interaction has been computed involving a nonempirical mean-field approach. On the basis of these calculations, we suggest that in the LOV domain the ISC takes place between the excited $^1(\pi \rightarrow \pi^*)$ state (S_1) and the $^3(n \rightarrow \pi^*)$ state (T_2). In aqueous solution this ISC channel is not accessible due to the blue shift of the $^3(n \rightarrow \pi^*)$ state.

MO 11.3 Mo 14:30 6B

Excitation Energy Transfer via Optically "Dark" States of Carotenoids in Photosynthetic Antenna Complexes investigated by Femtosecond Two-Photon Fluorescence Exciatation Spectroscopy — •Alexander Betke[1], Bernd Voigt[1], Heiko Lokstein[2], and Ralf Menzel[1] — [1]Institut für Physik, Lehrstuhl für Photonik, Universität Potsdam — [2]Institut für Biochemie und Biologie, Universität Potsdam

Carotenoids play several important roles in photosynthetic organisms: as integral structural components of pigment-protein-complexes, as light-harvesting pigments, and in photoprotection.
To study the last two mentioned functions and the underlying mechanism(s) it is vital to know the energetic positions of the lowest-lying excited singlet state, S_1 ($2^1A_g^-$) of relevant carotenoids. The latter states are assumed to be close to the (bacterio-)chlorophyll S_1 state. Due to their "optically forbidden" character, the carotenoid S_1 state is difficult to investigate by conventional one-photon spectroscopy. However, the $1^1A_g^-$ to $2^1A_g^-$ transition is strongly two-photon allowed. Thus, simultaneous two-photon absorption of tuneable femtosecond near infrared pulses monitored by (bacterio-) chlorophyll fluorescence is a powerful approach to study the role of these "dark" states in excitation energy transfer and dissipation in light-harvesting complexes. We will present recent results obtained with different light-harvesting complexes and highlight advantages as well as possible pitfalls of this approach.
This research is supported by the DFG (SFB 429, TP A2).

MO 11.4 Mo 14:45 6B

Elektronentransfer im photosynthetischen Reaktionszentrum: Optimierung in Modell und Natur — •Benjamin Fingerhut[1], Wolfgang Zinth[2] und Regina de Vivie-Riedle[1] — [1]Department Chemie, LMU, Butenandtstr. 11, 81377 München — [2]BMO, Sektion Physik, LMU, Oettingenstr. 67, 80538 München

Die Photosynthese als wichtigster Energiekonversionsschritt in der belebten Natur wurde im Zuge der Evolution über viele Jahrmillionen optimiert. Für ein verbessertes Verständnis dieser Vorgänge wurde ein theoretisches Modellsystem entwickelt, in dem der photosynthetische Elektronentransfer im bakteriellen Reaktionszentrum nachgebaut wurde. Das Simulationssystem berücksichtigt die wichtigsten Randbedingungen des Proteins. Mit Hilfe eines genetischen Algorithmus wurden relevante Parameter der mehrstufigen Transferkette optimiert. Die Untersuchungen zeigen die Bedeutung der verschiedenen molekularen Parameter für die Funktion des Reaktionszentrums. Die im Optimierungsprozess gefundenen Parametersätze werden mit aus Experimenten bekannten Informationen verglichen und zeigen für einen vorgegebenen Organismus in wesentlichen Bereichen eine gute Übereinstimmung. Das Auftreten von optimalen Parameterkonstellationen die nicht in der Natur realisiert sind wurde untersucht.

MO 11.5 Mo 15:00 6B

Towards the structure-selective measurement of exited state dynamics in DNA clusters — •Yuliya Rulyk[1], Elena Samoylova[1], Thomas Schultz[1], Hans-Hermann Ritze[1], Wolfgang Radloff[1], and Ingolf-Volker Hertel[1,2] — [1]Max Born Institute, Max-Born Strasse 2a, D-12489, Berlin, Germany — [2]Fachbereich Physik, Freie Universität Berlin, Arnimallee 14, D-14195, Berlin, Germany

Femtosecond pump-probe mass and electron spectroscopy is a powerful method for studying ultrafast exited state relaxation in DNA clusters. Nevertheless, this method has two substantial limitations. First, it is not selective with respect to different isomers of DNA clusters, which are expected to show different exited state dynamics. Second, the investigation of small clusters is impeded by fragmentation of bigger clusters.

To overcome the limitations mentioned, we develop an advanced method which combines ns hole-burning spectroscopy and time-resolved fs pump-probe mass spectroscopy. In this experiment, selected species are ionized by a ns UV pulse and removed from the active region of a spectrometer. The remaining species are characterized with fs pump-probe mass spectroscopy. We report on the progress and a first test of the experiment on indole-water clusters.

MO 11.6 Mo 15:15 6B

X-ray photoelectron spectroscopy of amino acids in aqueous solution — •Dirk Nolting[1], Manfred Faubel[2], Ingolf-Volker Hertel[1], and Bernd Winter[1] — [1]Max-Born-Institut für Nichtlineare Optik und Kurzzeitspektroskopie, Berlin, Deutschland — [2]Max-Planck-Institut für Dynamik und Selbstorganisation, Göttingen, Deutschland

The effect of solvation and protonation on the N 1s and C 1s core levels of amino acids was studied. For this a water beam was injected into a vacuum chamber and crossed with a synchrotron radiation beam. By varying the pH of the solution, different charge states could be addressed which made it possible to study protonation effects on nitrogen and adjacent carbons. Protonation caused a shift of 2 eV of N 1s to higher binding energies and a significantly smaller shift of 0.3 eV to adjacent carbon atoms.

MO 11.7 Mo 15:30 6B

Enantiomeric dependence of the THz spectra of polycrystalline Tyrosine and Valine — •Konstanze Schröck[1], Alan B. True[2], Timothy A. French[2], Martina Havenith[1], and Charles

A. Schmuttenmaer[2] — [1]Institute of Physical Chemistry II, Ruhr-University Bochum, Universitatsstr. 150, 44780 Bochum, Germany — [2]Yale University, Department of Chemistry, PO Box 208107, 225 Prospect St., New Haven, CT 06520-8107, USA

We used Terahertz Time-Domain Spectroscopy (THz TDS) to investigate the far-infrared absorption features of the two amino acids tyrosine and valine. The THz radiation was generated on a ZnTe(110) crystal by a regeneratively amplified Ti:Sapphire laser (repetition rate of 1 kHz, wavelength of 800 nm, 100 fs pulses with an energy of 1 mJ). The polycrystalline samples were pressed into pellets with a thickness of 0.25-0.5 mm. They were placed in a cryostat and spectra were taken under vacuum at room temperature and at 77 K. Furthermore, a temperature-dependent study of valine in the range of 77 to 290 K was undertaken. The absorption spectra of both the D and L enantiomers, as well as the DL racemates in the range of 0.1 to 2.5 THz will be presented. We show that the vibrational spectra of the D and L enantiomers are identical, but differ from the racemic mixtures. For all samples, the absorption maxima were found to be red-shifted as a function of increasing temperature. Furthermore, a computational study (CHARMM) was used to identify the molecular motions observed in the spectra. The vibrational modes are more intermolecular than intramolecular in character due to the hydrogen-bonding network.

MO 11.8 Mo 15:45 6B

PH Enhancement on the Adsorption Reaction of Nanodiamond/Nanosilica and Lysozyme Molecule — •Victor Wei-Keh Wu — Department of Chemical and Material Engineering, National Kaohsiung University of Applied Sciences, 80782 Kaohsiung, Taiwan — Group 510, Institute of Atomic and Molecular Sciences, Academia Sinica, P.O.Box 23-166, 10617 Taipei, Taiwan — Victor Basic Research Laboratory e. V. Gadderbaumer-Str. 22, 33602 Bielefeld, Germany, Email:victorbres3tw@yahoo.com.tw, http://www.che.kuas.edu.tw

Fluorescences from free lysozyme of 0-1000 nM in 7 mM PPBS at pH = 7, 9, 11 and 13 after adsorption reactions on the surfaces of nanodiamond/-silica (d≈100 nm, 5 μg/2.02 mL) with Xe lamp as light source monochromated at 285 nm of ca. 0.6 mW and PMA-11 of Hamamatsu as fluorescence spectrometer have been measured. Coverages as well as adsorption reaction constants (e.g. 1.6 x 10^8/4.5 x 10^7 $[nM]^{-1}$ for nanodiamond/-silica, respectively, at pH = 11) have been further obtained. Their quotients for both systems at pH = 7 - 13 is ca. 4. The max. appears at around 11 - 13, where lysozyme as "neutral" (pI≈11.5) can be easierly adsorbed. The available surface areas of nanodiamond and -silica during adsorption for each lysozyme can be estimated as 10 and 2 nm^2, respectively. Comparing this ratio with the quotients of the measured adsorption reaction constants, roughness of particle surface may also be decisive besides charge on and modification of the surface, pH of the surrounding for higher adsorption capability. The adsorbed lysozyme on the surface of nanodiamond may better keep its helicity as well as its activity. **Ref.** V. W.-K. Wu, Chem. Lett. 35, 1380 (2006)

MO 12: Femtosecond Spectroscopy I

Zeit: Montag 14:00–15:15 Raum: 6D

MO 12.1 Mo 14:00 6D

Coulomb Explosion Imaging of Molecular Hydrogen Anions — •Brandon Jordon-Thaden[1], Simon Altevogt[1], Dennis Bing[1], Max Berg[1], Henrik Buhr[1], Robin Golser[2], Huebert Gnaser[3], Oded Heber[4], Jens Hoffman[1], Holger Kreckel[1], Michael Lange[1], Mario Mendes[1], Oldrich Novotny[1], Steffen Novotny[1], Henrik Pedersen[1], Annemieke Petrignani[1], Hillel Rubinstein[4], Dirk Schwalm[1], Dror Shafir[4], Andreas Wolf[1], and Daniel Zajfman[1,4] — [1]Max-Planck-Institut für Kernphysik, Heidelberg, Germany — [2]VERA Laboratory, Universität Wien, Wien, Austria — [3]University of Kaiserlautern, Kaiserlautern, Germany — [4]Department of Particle Physics, Weizmann Institute of Science, Rehovot, Israel

With the recent confirmation of the existence of H_2^- and its isotopologues, foil-induced Coulomb Explosion Imaging (CEI) offers a unique and straightforward method to investigate the fundamental structure of the molecular anion characterized by a lifetime on the order of 10 microseconds, large internuclear separations, and large angular momentum quantum numbers. Using an energetic (500 keV/amu) beam and the sub-femtosecond stripping of the molecule in an 5 nm thick diamond-like carbon foil, the total kinetic energy release (KER) of the subsequent Coulomb explosion is determined by event-by-event imaging of the fragments about 2 m downstream. Accounting for effects induced by the foil and the initial, substantial rotational energy, we find the distribution of internuclear distances of the metastable ion. Results will be presented for measurements of H_2^- and D_2^-.

MO 12.2 Mo 14:15 6D

Theoretical analysis of high-order harmonic generation in complex molecules — •Marcelo Ciappina[1], Agnieszka Jaron-Becker[2], and Andreas Becker[1] — [1]Max-Planck-Institut für Physik komplexer Systeme, Nöthnitzer Str. 38, D-01187 Dresden, Germany — [2]Institut für Physikalische Chemie und Electrochemie, Technische Universität Dresden, D-01062 Dresden, Germany

The interaction of complex molecules with strong lasers has opened a new scenario to study many-body electronic systems. Due to the multicenter nature of the molecular species, new phenomena appear as a consequence of the nonperturbative character of the interrelation between coherent electromagnetic radiation and such collection of atoms (e.g. [1]). In order to study the dependence of high-order harmonics on the molecular structure and orientation, molecules have to be prealigned prior to the actual strong-field interaction. Such alignment was performed in recent experiments where a combination of an aligning picosecond pulse and an intense femtosecond pulse was used [2]. In this work we present results for High-order Harmonic Generation (HHG) on complex molecules using the Strong Field Approximation (SFA) or Lewenstein model [3]. Using different types of molecules, we emphasize features relating to the interference patterns that appear as a consequence of the their multicenter nature. We show the differences among randomly and oriented molecules using a standard average procedure. [1] A. Jaroń-Becker *et al*, Phys. Rev. Lett. **96** 143006 (2006). [2] J. Itatani *et al*, Phys. Rev. Lett. **94** 123902 (2005). [3] M. Lewenstein *et al*, Phys. Rev. A **49** 2117 (1994).

MO 12.3 Mo 14:30 6D

Ultraschnelle Zerfallsdynamik von Rydberg-Zuständen des CS_2 — •Andreas Wirsing[1], Jürgen Plenge[1], Manuel Krug[2] und Eckart Rühl[1] — [1]Physikalische und Theoretische Chemie, Institut für Chemie und Biochemie, Freie Universität Berlin, Takustr. 3, 14195 Berlin — [2]Institut für Physikalische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

Kohlenstoffdisulfid (CS_2) ist Gegenstand zahlreicher Untersuchungen zur ultraschnellen Zerfallsdynamik im Femtosekundenbereich, wobei der $^1B_2(^1\Sigma_u^+)$-Valenzzustand von besonderem Interesse ist [1]. Dieses besondere Interesse ergibt sich aus der signifikanten Abhängigkeit der Prädissoziations-Lebensdauer dieses Zustands von der primären Anregungswellenlänge. Es gibt dagegen nur wenige Untersuchungen zur ultraschnellen Zerfallsdynamik von höher angeregten Rydberg-Zuständen des CS_2.

Wir präsentieren Ergebnisse zur ultraschnellen Zerfallsdynamik des 4f-Rydberg-Zustands von CS_2, die mit Hilfe der zeitaufgelösten Mehrphotonen-Ionisations-Massenspektrometrie (Pump: 402.5 nm; Probe: 805 nm) erzielt wurden. Die Lebensdauer des angeregten 4f-Rydberg-Zustands wird für die beiden Isotopomere $C^{35}S^{35}S$ und $C^{37}S^{35}S$ aus der Zeitabhängigkeit der jeweiligen Massensignale abgeleitet. Die Resultate werden im Zusammenhang mit Ergebnissen früherer Untersuchungen [1] zur Zerfallsdynamik von Rydberg-Zuständen des CS_2 diskutiert.

[1] I.V. Hertel und W. Radloff, Rep. Prog. Phys. 69,1897 (2006).

MO 12.4 Mo 14:45 6D

Antisymmetric molecular orbitals and magnetic-field effects in intense laser fields — •Robert Fischer[1], Manfred Lein[1,2], and Christoph H. Keitel[1] — [1]Max-Planck-Institut für Kernphysik, Heidelberg — [2]Institut für Physik, Universität Kassel

This talk points out a recently discovered mechanism to enhance recollision-related effects like high-harmonic generation by combining

the properties of antisymmetric molecular orbitals and the drift induced by the laser magnetic field [1]. In order to investigate the interplay of the two drifts with regard to high-harmonic generation we present results obtained by the direct numerical solution of the time-dependent Schrödinger equation for a scenario in which an antisymmetric wavefunction is subject to a very intense short laser pulse. To take the notable magnetic field drift into account the simulations have been performed without applying the dipole approximation for the laser field. As a result of the combination of both effects a dramatic enhancement of the harmonic signal by several orders of magnitude has been observed.

[1] R. Fischer, M. Lein, and C. H. Keitel, Phys. Rev. Lett. **97**, 143901 (2006).

MO 12.5 Mo 15:00 6D

Kontrolle des Produktverhältnisses in der Photofragmentierung von DCl+ — Hans Georg Breunig, Gunther Urbasch, Mikhail Korolkov und •Karl-Michael Weitzel — Fachbereich Chemie, Philipps Universität Marburg, 35032 Marburg

Die Photofragmentierung von DCl+ Ionen führt alternativ zur Bildung von D+ + Cl oder Cl+ + D in konkurrierenden Reaktionskanälen. Das Verzweigungsverhältnis D+ / Cl+ wurde einerseits theoretisch durch Lösung gekoppelter zeitabhängiger Schrödinger-Gleichungen anderseits experimentell mit Hilfe der fs dissoziativen Ionisation von DCl. Die theoretische Studie zeigt ein stufenartiges Anwachsen des Verzweigungsverhältnisses bei Intensitäten, die charakteristisch von den Anfangschwingungszuständen bei nicht-resonanter Multiphotonenanregung abhängen. Im allgemeinen sinkt die Schwelle mit zunehmender Schwingungsquantenzahl. Unsere experimentellen Studien zeigen ein ähnliches stufenartiges Verhalten des Verzweigungsverhältnisses. Hier hängt die Intensität, bei der die Stufe beobachtet wird, deutlich vom chirp des fs-Lasers ab. Dies legt nahe, daß unterschiedlicher chirp zu intermediären Ionen mit unterschiedlicher effektiver Schwingungsquantenzahl führt. Die Rolle von Schwingungswellenpaketen wird diskutiert.

MO 13: Photochemistry

Zeit: Montag 16:30–18:45 Raum: 6B

MO 13.1 Mo 16:30 6B

Beeinflussung der Ringöffnungsdynamik eines Indolylfulgids — •Florian Lederer[1], Simone Draxler[1], Thomas Brust[1], Stephan Malkmus[1], Jessica A. DiGirolamo[2], Watson J. Lees[2], Wolfgang Zinth[1] und Markus Braun[1] — [1]Ludwig-Maximilians-Universität München, Lehrstuhl für BioMolekulare Optik, Oettingenstr. 67, 80538 München — [2]Department of Chemistry and Biochemistry, Florida International University

Unter den molekularen Schaltern fällt die Gruppe der Indolyl-Fulgide/Fulgimide durch ihre ausgeprägte Photochromie und die Stabilität ihrer Isomere auf. Die Absorptionsspektren der zyklisierten und zyklisierbaren Isomere, die durch photoinduzierten Ringschluss bzw. Ringöffnung ineinander überführt werden können, unterscheiden sich durch getrennte Banden im sichtbaren und ultravioletten Spektralbereich.

Durch Dauerstrich- und Femtosekunden-Pump-Probe-Spektroskopie wurden sowohl die Reaktionsausbeute als auch die Reaktionsdynamik der Ringöffnung untersucht. Sie lassen sich durch eine Vielzahl von Parametern beeinflussen: Während die Viskosität des Lösungsmittels keinen Effekt auf die Ausbeute hat, kann durch die Erhöhung des Dipolmoments die Ausbeute der Ringöffnungsreaktion deutlich reduziert werden. Die Auswirkungen einer Temperaturänderung weisen auf eine aktivierte Photoreaktion hin.

MO 13.2 Mo 16:45 6B

Photochemische Reaktionspfade nach Anregung in unterschiedliche elektronische Zustände: fluorierte Indolyl-Fulgide — •Simone Draxler[1], Stephan Malkmus[1], Thorben Cordes[1], Thomas Brust[1], Jessica A. DiGirolamo[2], Watson J. Lees[2], Wolfgang Zinth[1] und Markus Braun[1] — [1]LS für BioMolekulare Optik, LMU München — [2]Depmt. of Chem. and Biochem., FIU Miami, USA

Nach der Kasha-Regel beobachtet man Fluoreszenz im allgemeinen aus dem niedrigsten angeregten Zustand, unabhängig vom ursprünglich angeregten Zustand. Dies setzt eine ultraschnelle Relaxation vom S_n in den S_1 voraus. Auch für photochemische Prozesse wurde dieser Reaktionsweg aus dem S_1 in vielen Untersuchungen bestätigt, wenn auch Ausnahmen dazu auftreten (z.B. Azobenzol [1]). Als weitere Ausnahme von dieser Regel wird hier ein spezielles Fulgid vorgestellt.

Mittels transienter Absorptionsspektroskopie wurden die Reaktionspfade bei Anregung in den S_1 sowie S_2 des fluorierten Indolyl-Fulgids untersucht. Bei der Ringschlussreaktion wurde keine wesentliche Abweichung vom herkömmlichen Bild einer der Reaktion vorgeschalteten internen Konversion in den S_1 gefunden. Die UV-induzierte (S_2) Ringöffnungsreaktion hingegen weist einen anderen Reaktionspfad als die sichtbar induzierte (S_1) Reaktion auf. Dies spiegelt sich auch in der Vervierfachung der Quanteneffizienz wider (S_1: 7%; S_2: 28%).

[1] H. Satzger et al., J. Phys. Chem. A **108**, 6265, (2004)

MO 13.3 Mo 17:00 6B

Photodissociation of Uracil — •Michael Schneider[1], Christof Schon[1], Luis Rubio-Lago[2], Bastian Noller[1], Theofanis Kitsopoulos[2], and Ingo Fischer[1] — [1]Institut für Physikalische Chemie, Julius-Maximilians-Universität Würzburg, Am Hubland, 97074 Würzburg, Germany — [2]Institute of Electronic Structure and Laser, Foundation for Research and Technology-Hellas (FO.R.T.H.), P.O. Box 1527, 71110 Heraklion, Crete, Greece

We examined the photodissociation of uracil after UV excitation by H-atom photofragment Doppler spectroscopy and slice imaging. The kinetic energy distribution shows a behaviour typical for statistical dissociation. No anisotropy is observed in the angular distribution of the images. Thus the photodissociation is purely statistical and there is no evidence for the contribution of repulsive $\pi\sigma^*$-states as is the case in adenine.

MO 13.4 Mo 17:15 6B

Intersystem Crossing Driven by Vibronic Spin-Orbit Coupling: A Case Study on Psoralen — •Jörg Tatchen, Martin Kleinschmidt, and Christel Marian — Institute of Theoretical Chemistry, Heinrich-Heine University, Universitätsstraße 1, D-40225 Düsseldorf

Psoralens are used in combination with UVA radiation in the treatment of several skin diseases. In order to understand the mechanisms behind the therapeutical action and undesired side effects, insight into the photophysics of psoralens is highly desirable. By means of quantum chemical methods, we investigate the mechanisms of singlet-triplet ($S \rightsquigarrow T$) intersystem crossing (ISC) in photoexcited psoralen.

Our results [1,2,3] show that the dominant channel of $S \rightsquigarrow T$ ISC for psoralen is $S_1\,(\pi \rightarrow \pi^*) \rightsquigarrow T_1(\pi \rightarrow \pi^*)$ even though the corresponding spin-orbit matrix element (SOME) $\langle S_1|\mathcal{H}_{\mathrm{SO}}|T_1\rangle$ at the planar S_1 state equilibrium geometry is negligible. Efficient $S_1 \rightsquigarrow T_1$ ISC takes place due to vibronic spin-orbit coupling which is included by a Herzberg-Teller type expansion of the coupling SOMEs. In addition, a conical intersection between the S_1 and T_1 state potential energy surfaces near the S_1 minimum geometry brings about favorable Franck-Condon factors for the $S_1 \rightsquigarrow T_1$ ISC.

References

[1] Tatchen, J.; Kleinschmidt, M.; Marian, C. M.: *J. Photochem. Photobiol. A*, 167, 201-212 (2004).

[2] Tatchen, J.; Marian, C. M.: *Chem. Phys. Phys. Chem.* , 8, 2133-2144 (2006).

MO 13.5 Mo 17:30 6B

Femtosecond Experiments on the Photochemistry of Organic N-Oxides — •Nadja Regner, Thorben Cordes, Tobias Schrader, and Peter Gilch — Lehrstuhl für BioMolekulare Optik, Department für Physik, Ludwig-Maximilians-Universität München, Oettingenstr. 67, 80538 München

The photo-rearrangement of organic N-oxides is a useful synthetic tool to synthesize chemicals which are difficult to access by other methods. Therefore, a large variety of N-oxides have been tested for photoreactivity and in most cases these tests turned out positive [1]. In contrast to this wealth of empirical information our knowledge of the

mechanisms of these reactions is poor. In particular, no spectroscopic experiments with a suitable time resolution have yet been published. We here report on a combined femtosecond UV/Vis and IR study on the rearrangement of an N-oxide (2-benzoyl-3-phenylquinoxaline-1,4-dioxide). This rearrangement results in large structural changes which involve several elementary steps occurring with time constants of a few picoseconds to beyond nanoseconds. Based on the femtosescond IR signatures reactions associated with these times constants are suggested.
[1] A. Albini and M. Alpegiani Chem. Rev. 84 (1984) 43

MO 13.6 Mo 17:45 6B

Precursor molecules for organic synthesis: A model system for initial dissociation dynamics of diphenylmethylchloride — •Benjamin Fingerhut, Dorothee Geppert, and Regina de Vivie-Riedle — LMU Department Chemie, Butenandt-Str. 11, 81377 München, Germany

Our investigations focus on the laser induced dissociation dynamics of diphenylmethylchloride and its derivatives which occur on a femtosecond timescale. An understanding of the initial fragmentation pathways gives insight into the formation of carbo-cations in solution, key intermediates in organic synthesis.

For an accurate description of the excitation and the dissociation process at least three electronic states have to be taken into account by quantum chemical methods. A π^* - σ^*-charge-transfer connects the Franck-Condon region with a repulsive potential, followed by nonradiative relaxation into the competing reaction channels. The branching ratio between the bound and the repulsive fragmentation pathway is facilitated by at least one conical intersection and defined by appropriate non-adiabatic-coupling-matrix-elements.

We present a model system, based on our ab-initio data which is suitable to describe the multidimensional dissociation process in a reduced reactive coordinate subspace. Herein we are able to follow the dissociation dynamics via multiple conical intersections after femtosecond laser excitation.

MO 13.7 Mo 18:00 6B

Singlet Oxygen generation from Aromatic Endoperoxides — •Alexandra Lauer[1], Inés Corral[2], Leticia González[2], Henk Fidder[1], and Karsten Heyne[1] — [1]Freie Universität Berlin, Fachbereich Physik, Arnimallee 14, 14195 Berlin — [2]Freie Universität Berlin, Fachbereich Chemie, Takustrasse 3, 14195 Berlin

Aromatic endoperoxides are claimed to exhibit homolytic cleavage from the lowest electronic excited state, while higher electronic states lead to singlet oxygen generation. However, this lowest electronic state has never been located, and recent semi-empirical calculations even denied the existence of this state. In our contribution state-of-the-art ab initio calculations are combined with steady-state absorption and fluorescence experiments, and polarization-resolved femtosecond UV-pump/IR-probe spectroscopy, to resolve this issue. We observe the disputed S1 state of APO that leads to homolytic O-O cleavage, at 33700 cm^{-1}, in excellent agreement with our ab initio calculations. Femtosecond polarization resolved UV/IR experiments confirm that the absorption transition dipole at 36800 cm^{-1} is indeed polarized parallel to the oxygen bridge, thereby verifying the theoretical assignment of this band to the S0→S4 transition. A mechanism for $^1O_2$ generation from APO is presented, based on the ab initio calculations, that indicates how excitation to the S2 ($\pi_{CC} \rightarrow \pi^*_{CC}$) or S4 ($\pi^*_{OO} \rightarrow \pi^*_{CC}$) state leads to non-adiabatic population of the Sx ($\pi^*_{OO} \rightarrow \sigma^*_{CO}$) state, which plays a decisive role in the $^1O_2$ generation.

MO 13.8 Mo 18:15 6B

H-transfer reaction in 2-aminopyridine dimer studied by fs pump-probe spectroscopy — •Elena Samoylova[1], Yuliya Rulyk[1], Dirk Nolting[1], Hans-Hermann Ritze[1], Wolfgang Radloff[1], Ingolf Volker Hertel[2], and Thomas Schultz[1] — [1]Max Born Institute, Max-Born Str.2A, Berlin, Germany — [2]Freie Universität Berlin, Fachbereich Physik, Arnimallee 14, Berlin, Germany

H-bonded intermolecular interactions play a very important role in the biophysics of DNA, determining its structure and dynamics. For the electronically excited states, theory predicted a very fast deactivation mechanism involving H-transfer along the N-H coordinate in DNA base pairs. This mechanism can quench highly reactive excited states and provide the necessary photostability against photoinduced damage for the genetic information. We studied the H-transfer mechanism in 2-aminopyridine dimer, a model system for H-bound Watson-Crick DNA base pairs. Using time-resolved ion and electron spectroscopy we identified a fast deactivation pathway of the excited state (life time is 69 ps at 274 nm). Higher vibrational excitation at 250 nm lead to a slight increase of the life time to 75 ps, and we observed an additional ultrafast (less then 50 fs) deactivation channel. The ultrafast contribution can be explained by the initial wave packet motion along N-H stretching mode carrying part of the population over the H-transfer barrier. The remaining population is caught in the local minimum and decays on the ps time scale.

MO 13.9 Mo 18:30 6B

Photochemistry inside superfluid helium nano droplets — •Alkwin Slenczka, Alexander Vdovin, and Bernhard Dick — Institut für Physikalische und Theoretische Chemie, Universität Regensburg, 93053 Regensburg, Germany

Superfluid helium nano droplets serve as the most gentle cryogenic matrix for creating isolated and cold molecules [1]. High resolution electronic spectroscopy is sensitive for the investigation of the very weak perturbation of the helium droplet on the embedded molecule. Fluorescence excitation spectra, dispersed emission spectra and pump-probe-spectra show details of the salvation of molecules in helium droplets which were attributed to relaxation processes of the first solvation layer around the dopant [2]. Photochemistry such as ESIPT, tautomerization by proton transfer and charge transfer are highly sensitve on intermolecular perturbations. We have studied such processes in superfluid helium droplets. The comparison with the respective gas phase experiments and quantum chemical calculations reveals further details on the photochemistry as well as on the perturbation by the superfluid helium droplet.

[1] F. Stienkemeier, K. K. Lehmann, J. Phys. B: Mol. Opt. Phys. 39(2006) R127-R166.

[2] R. Lehnig, and A. Slenczka, J. Chem. Phys. 123, (2005).; Chem. Phys. Chem. 5, (2004) 1013-1019; J. Chem. Phys. 120, (2004), 5064-5066; J. Chem. Phys. 118, (2003) 8256-8260.

MO 14: Molecular Clusters

Zeit: Montag 16:30–18:00 Raum: 6D

MO 14.1 Mo 16:30 6D

MD simulations of laser excited clusters — •Thomas Raitza, Heidi Reinholz, and Gerd Roepke — Universität Rostock; Universitätsplatz 3; 18055 Rostock

The measurements of optical properties are relevant for plasma diagnostics. The investigation of reflectivity and absorption of electromagnetic waves in inhomogeneous media will be done with special attention to laser excited clusters. Interaction of cluster systems with intense laser pulses were investigated via MD simulation. Hydrogen and sodium clusters containing 50 - 500 atoms were calculated. Material properties were included using and discussing different pseudo potentials. Comparison to experimental absorption measurements of Kim et al. [1] and to simulations of Belkacem et al. [2], Ditmire et al. [3] and Fennel et al. [4] are shown.

[1] K. Y. Kim, I. Alexeev, E. Parra, and H. Milchberg; *PRL*, **90**, 023401 (2003)

[2] M. Belkacem, F. Megi, and E. Suraud; *Eur. Phys. J. D*, **40**, 247 (2006)

[3] T. Ditmire, T. Donnelly, A. M. Rubenchik, R. W. Falcone, and M. D. Perry; *PRA*, **53**, 3379 (1996)

[4] T. Fennel, G. F. Bertsch, and K.-H. Meiwes-Broer; *Eur. Phys. J. D*, **29**, 367 (2004)

MO 14.2 Mo 16:45 6D

Master Equation Modeling of Phase Transitions in Low Tem-

perature Black-Body Infrared Radiative Dissociation (BIRD) of Hydrated Ions — Stephan J. Reitmeier[1], O. Petru Balaj[2], Mirko Gruber[1], and •Martin K. Beyer[3] — [1]Department Chemie, TU München, Germany — [2]DCMR-Ecole Polytechnique, Palaiseau, France — [3]Insitut für Chemie, TU Berlin, Germany

Black-body infrared radiative dissociation (BIRD) of $V(H_2O)_n^+$, $n = 5$ - 21, was studied with a newly developed temperature-controlled ICR cell in a temperature range of 200 - 300 K. Arrhenius plots of the observed unimolecular rate constants for the loss of water molecules exhibit the expected linear behavior, which confirms that the radiation temperature experienced by the trapped ions actually is the measured temperature of the cell walls. Analysis with the standard master equation modeling of a single reactant well yields activation energies for the loss of water molecules which are significantly lower than those calculated with density functional theory or literature values of the water binding energy to protonated water clusters. Ab initio molecular dynamics simulations of selected cluster sizes reveal that some hydrogen bonds which are present in the equilibrium geometry are broken at elevated temperatures. The energy of those hydrogen bonds is present as latent heat in the clusters, which helps to lower the activation energy of water loss. A multi-well master equation model is developed to describe the population of the different phases in the trapped ensemble of ions. Activation energies derived from single and multi-well master equation modeling are compared.

MO 14.3 Mo 17:00 6D

IR Spectra of Protonated Furan, Pyrrole, and Naphthalene — •Ulrich Lorenz[1], Joel Lemaire[2], Philippe Maitre[2], Maria-Elisa Crestoni[3], Simonetta Fornarini[3], and Otto Dopfer[1] — [1]Institut für Optik und Atomare Physik, Technische Universität Berlin, Berlin, Germany — [2]Laboratoire de Chimie Physique, UMR8000 CNRS-Université Paris-Sud 11, Faculté des Sciences d' Orsay, Orsay Cedex, France — [3]Dipartimento di Studi di Chimica e Tecnologia delle Sostanze Biologicamente Attive, Università di Roma La Sapienza, Roma, Italy

Infrared Multiple Photon Dissociation (IRMPD) Spectra of protonated furan, pyrrole, and naphthalene are recorded in the 700 to 1800 cm^{-1} range in order to probe the preferred site of protonation. The species are generated by chemical ionization of the corresponding neutral compounds in a ICR mass spectrometer and dissociated employing the free electron laser at the Centre Laser Infrarouge Orsay. The comparison with the linear IR spectra calculated at the B3LYP/6-311G(2df,2pd) level of theory allows for the assignment of the most stable isomers as the carriers of the observed spectral features. The spectrum of protonated naphthalene is discussed in the context of the hypothesis that protonated polycyclic aromatic molecules (PAHs) might contribute to the astronomically observed Unidentified Infrared Emission (UIR) Bands.

MO 14.4 Mo 17:15 6D

Orbital-Dependent Stabilization in the Ionization of CS_2 Cluster — •Jürgen Plenge[1], Takaki Hatsui[2], Nobuhiro Kosugi[2], and Eckart Rühl[1] — [1]Physikalische und Theoretische Chemie, Institut für Chemie und Biochemie, Freie Universität Berlin, Takustr. 3, 14195 Berlin — [2]Institute for Molecular Science, Myodaiji, Okazaki, 444-8585, Japan

Molecular van der Waals clusters offer the opportunity to study the gap between the isolated molecule and condensed matter. It is known that the formation of clusters leads to a decrease in the ionization energy with respect to the molecule, which is commonly interpreted in terms of final state polarization due to the created hole. In the case of valence ionization of molecular clusters, the created holes are generally delocalized within the molecule, where the shape of the hole is characteristic for the molecular valence orbital.

We present results on molecular orbital dependent stabilization of valence-ionized states in CS_2 clusters. Valence photoelectron spectra of isolated CS_2 molecules and CS_2 clusters are measured using synchrotron radiation (UVSOR-II, beamline BL3U) and a He-I discharge lamp. The experimental spectra indicate a shift of the molecular photoelectron bands in the cluster between 0.55 eV (ground state) and 0.70 eV (C state) to lower binding energy. These results are compared to results on CO_2 clusters and they are discussed in terms of a molecular orbital dependent stabilization of the final ionic states in molecular clusters, where ionized states with the lower binding energies are found to show a smaller stabilization effect.

MO 14.5 Mo 17:30 6D

Laserspektroskopie massenselektierter Ion-Molekülcluster: Chlorid-Anionen in Ammoniak — •Martin Tschurl und Ulrich Boesl — TU München, Department Chemie, Physikalische Chemie 1, Lichtenbergstraße 4, D-85748 Garching

Die Solvatation von Ionen spielt eine zentrale Rolle in verschiedensten Gebieten der Chemie und Physik. Durch das Studium kleiner Komplexe erhofft man sich, theoretische Modelle verfeinern und schlussendlich Effekte in Lösung besser erklären zu können.

Die Anionen-Photoelektronenspektroskopie (PES), die Photodetachmentspektroskopie (PDS) und die IR-Dissoziationsspektroskopie (IR-DS) zählen hierbei zu den leistungsstärksten Methoden bei der Untersuchung solcher Komplexe. Unsere Apparatur erlaubt nun erstmals die Kombination dieser drei Methoden. So ist gewährleistet, dass die Komplexe bei denselben Bildungsbedingungen studiert werden.

Anhand des kleinsten Chlorid-Ammoniak Komplexes soll exemplarisch das Zusammenspiel von PDS und IR-DS gezeigt werden. Beide Methoden liefern neue Erkenntnisse über diesen Komplex. Da keine Spektren von Chlorid Komplexen mit mehreren Ammoniakmolekülen in der Literatur vertreten sind, wurden diese mittels IR-DS untersucht. So konnten Informationen von Komplexen bis zu einer Größe von vier Ammoniakmolekülen pro Chloridion erhalten werden, die Aussagen über die involvierten Komplexgeometrien liefern.

MO 14.6 Mo 17:45 6D

Photoelectron spectroscopy of molecular diamonds — •Kathrin Klünder[1], Christoph Bostedt[1], Tobias Richter[1], Lasse Landt[1], Peter Zimmermann[1], Thomas Möller[1], Trevor Willey[2], Tony van Buuren[2], Jeremy Dahl[3], SG Liu[3], and Robert Carlson[3] — [1]TU Berlin, Germany — [2]LLNL, Livermore CA, USA — [3]MolecularDiamond Technologies, Richmond CA, USA

Diamondoids are ideal molecular diamond clusters. They are perfectly size- and isomer-selected, neutral and hydrogen-terminated clusters in the diamond bulk lattice configuration. Diamondoids are a perfect system for investigating the electronic properties of semiconductor nanostructures in the molecular limit.

First x-ray absorption experiments of diamondoids showed no particle size dependence of the lowest unoccupied states which has been confirmed by quantum monte carlo simulations. In contrast to the unoccupied states, however, the calculations predict strong quantum size effects in the occupied states.

We have studied the highest molecular orbitals and core levels of a series of diamondoids by means of photoelectron spectroscopy. The experiments were performed at the beamline UE56/2 of the Bessy synchrotron source with a Scienta hemispherical photoelectron analyser. The valence band photoelectron spectra show a clear energy shift of the highest molecular orbitals to lower binding energies for increasing particle size. The results will be discussed and compared to recent theory.

MO 21: Femtosecond Spectroscopy II

Zeit: Dienstag 10:30–12:30 Raum: 6D

Fachvortrag MO 21.1 Di 10:30 6D

Ab initio simulations of linear and nonlinear infrared spectroscopy — •Jens Dreyer — Max-Born-Institut für Nichtlineare Optik und Kurzzeitspektroskopie, Max-Born-Strasse 2A, D-12489 Berlin, Germany

Vibrational excitations play a central role for the ultrafast nonequilibrium dynamics of intra- and intermolecular hydrogen bonds. The stretching vibration of hydrogen-bonded O-H and N-H groups undergoes pronounced changes of frequency and vibrational line shape upon hydrogen bonding and frequently displays subpicosecond population lifetimes, which are much shorter than the corresponding lifetimes of free O-H/N-H groups. Relaxation via fingerprint mode overtone and combination bands mediated by Fermi resonance coupling as well a decay into low-frequency hydrogen bond modes have been invoked to explain such short lifetimes.

It will be shown how density functional theory calculations of anharmonic couplings in hydrogen bonds are used to address the linear and nonlinear vibrational spectroscopy of hydrogen bonds [1]. We predict and analyze multidimensional signatures of hydrogen bond coupling mechanisms by ab initio simulations of 2D IR spectra. The particular case of acetic acid dimers will be presented [2]. We address the lifetime shortening of 7-azaindole N-H stretching excitations in going from the monomer to the dimer as well as the mechanisms underlying the complex substructure of the N-H stretching infrared absorption band.

[1] J. Dreyer J. Chem. Phys. 2005, 122, 184306 ; [2] J. Dreyer Int. J. Quantum Chem. 2005, 104, 782.

MO 21.2 Di 11:00 6D

Ultrafast dynamics of vibrational N-H stretching excitations in the 7-azaindole dimer — •Jason R. Dwyer, Jens Dreyer, Erik T. J. Nibbering, and Thomas Elsaesser — Max Born Institut für Nichtlineare Optik und Kurzzeitspektroskopie, Max Born Strasse 2A, D-12489 Berlin, Germany

The ultrafast vibrational response of hydrogen bonds in the 7-azaindole dimer, a model compound for DNA base pairing, is studied in infrared pump-probe experiments. We observe a ˜ 100 fs relaxation of the v = 1 state of the N-H stretching oscillators via anharmonically coupled over- and combination tones of fingerprint modes. In the monomer with a larger energy mismatch between the v = 1 state and over-/combination tones, a much longer lifetime of 10 ps is found. Femtosecond N-H stretching excitation induces coherent underdamped motions of the dimer, dominated by the anharmonically coupled 110 cm-1 stretching mode of the hydrogen bonds.

MO 21.3 Di 11:15 6D

Femtosecond vibrational sum frequency generation in the fingerprint region — •Sylvie Roke — MPI for Metals Research, Heisenbergstrasse 3, 70569 Stuttgart, Germany

Second-order nonlinear optical techniques are well established tools to study interfaces. Infrared visible Sum Frequency Generation (SFG) is an extremely valuable tool, since it combines the surface specificity with the ability to probe vibrational degrees of freedom. When using femtosecond lasers one can access both structure and dynamics of the interface.

Such studies have been limited, however, by the availability of femtosecond infrared laser sources. Therefore, most femtosecond SFG studies (as well as most other femtosecond tecniques that employ infrared radiation) have been performed in the frequency region of 4000-1000 cm^{-1}.

The fingerprint region (1000-500 cm^{-1}) is a very interesting one since this region contains typically vibrational modes that are specific to the 3D-structure of molecules, and is very sensitive to molecular interactions. This has remained unexplored. Therefore, we report a table-top femtosecond Ti:Sa laser that produces high power laser pulses, which are converted into tunable infrared radiation. The system produces infrared pulses with a tuning range from 4000-500 cm^{-1} and a power of 110-11 mW. We also show it is possible to probe surface vibrational modes in the fingerprint region, with a femtosecond SFG experiment.

MO 21.4 Di 11:30 6D

Towards Femtosecond Stimulated Raman Microscopy (FSRM) — •Evelyn Plötz, Stefan Laimgruber, Stefan Berner, and Peter Gilch — Institut für BioMolekulare Optik, Department für Physik, Ludwig-Maximilians-Universität, Oettingenstr. 67, D-80538 München, Germany

Since the invention of microscopy diverse techniques to enhance the contrast of biological samples have been developed. In that respect, techniques relying on vibrational spectroscopy are very promising since the provide a contrast mechanism based on the chemical composition (chemical contrast). Because IR microscopy suffers from a low spatial resolution and (conventional) Raman microscopy from the low signal levels, non-linear Raman spectroscopy was applied for microscopy. Today the most important implementation is based on Coherent Anti-Stokes Raman Scattering (CARS) [1].

We here present a potential alternative to CARS microscopy, Femtosecond Stimulated Raman Microscopy (FSRM). In FSRM a femtosecond white light and narrow bandwidth laser pulse are focused onto the sample by a microscope objective. Stimulated Raman interaction superpose the Raman signature of the focal spot with the white light spectrum. By raster scanning the sample a FSRM micrograph can be recorded. Merits and pitfalls of FSRM in comparison with CARS microscopy will be discussed.

[1] J.-X. Cheng, X.S. Xie, J. Phys. Chem. B 108 (2004) 827

MO 21.5 Di 11:45 6D

Mode-Selective Excitation with Tailored Femtosecond Laser Pulses under Electronically Resonant and Nonresonant Excitation Conditions: The Role of Phase and Amplitude Modulation — •Jakow Konradi[1], Atila Gaál[2], Abraham Scaria[1], Vinu Namboodiri[1], and Arnulf Materny[1] — [1]International University Bremen (Jacobs University Bremen as of spring 2007), Germany — [2]International Laser Center, Bratislava, Slovak Republic

Coherent anti-Stokes Raman scattering (CARS) spectroscopy with femtosecond laser pulses is a powerful tool for the investigation of vibrational dynamics on an ultrashort time scale. However, the gain of temporal resolution entails a poor spectral resolution due to the inherent spectral width of the femtosecond excitation pulses. Recently, we have demonstrated that the nonlinear four-wave mixing signal extremely sensitively depends on the “chirp” of the exciting and probing pulses. The application of a self-learning loop approach for the optimal shaping of the femtosecond laser pulses allows for a relative (and absolute) enhancement or suppression of selected vibrational modes. Here, the ratio of signal intensities of different Raman lines observed in the CARS spectrum served as feedback signal for an evolutionary algorithm finding the best setting for the pulse shaper. While in our first experiments solely a modulation of the phases of the spectral pulse components was applied, in our present contribution we will discuss results obtained from an optimization varying phase as well as amplitudes. The optimization of the CARS spectra was performed both under electronically resonant and nonresonant excitation conditions.

MO 21.6 Di 12:00 6D

Symmetrieabhängige Solvatation bei Donor-substituierten Triarylboranen — •Uwe Megerle[1], Stefan Lochbrunner[1], Eberhard Riedle[1], Rainer Stahl[2] und Christoph Lambert[2] — [1]Lehrstuhl für BioMolekulare Optik, LMU München — [2]Institut für Organische Chemie, Universität Würzburg

Donor-substituierte Triarylborane (TABs) zeigen eine ausgeprägte Solvatochromie aufgrund der starken Veränderung und Umkehr des Dipolmoments bei Zustandswechseln. Bei dem eigentlich hochsymmetrischen dreifach Carbazol-substituierten TAB muss zusätzlich ein umgebungsinduzierter Symmetriebruch vorliegen [1]. Die Solvatation von TABs mit einem und drei Carbazol-Subchromophoren wurde anhand der Rotverschiebung der Emission in einem fs-Anrege-Abfrage-Experiment untersucht. Das dreiarmige TAB wird in dem vergleichsweise stark viskosen Benzonitril langsamer (8 ps) und in dem niedrig viskosen Chloroform schneller (1 ps) solvatisiert als das einarmige (jeweils 4-5 ps). Wir vermuten, dass sich je nach Viskosität das Dipolmoment im elektronisch angeregten symmetrischen TAB drehen kann. Bei hoher Viskosität bleibt der Symmetriebruch des Grundzustands erhalten und die Lösungsmitteldipole müssen sich entsprechend dem umge-

kehrten Dipolmoment des angeregten Zustands ausrichten. Bei niedriger Viskosität kann dagegen der Symmetriebruch aufgehoben werden und ein Anregungstransfer zwischen den Subchromophoren und eine schnellere Absenkung des angeregten Zustands stattfinden. Messungen des Anisotropiezerfalls unterstützen dieses Modell.

[1] R. Stahl et al., Chem. Eur. J. **12** (2006), 2358.

MO 21.7 Di 12:15 6D

Excited State Reaction Pathways of a Photo-induced Pericyclic Ring Opening and Closure — •Björn Heinz[1], Stephan Malkmus[1], Stefan Laimgruber[1], Steffen Dietrich[2], Christine Schulz[2], Karola Rück-Braun[2], Markus Braun[1], Wolfgang Zinth[1], and Peter Gilch[1] — [1]Department für Physik, Ludwig-Maximilians-Universität, Oettingenstr. 67, D-80538 München, Germany — [2]Institut für Chemie, Technische Universität Berlin, Str. d. 17. Juni, D-10623 Berlin, Germany

Many chemical reactions involving cyclic transition states obey the Woodward-Hoffmann rules. They make predictions on the occurrence and the stereochemistry of such reactions and can be applied for either direction of a chemical reaction – for instance a cyclisation and a cycloreversion. This suggests that both directions follow the same reaction path on the potential energy surface. For a photochemical cyclisation/cycloreversion of a fulgimide we present experimental evidence that this is not the case. We have recorded femtosecond fluorescence data for either direction and have observed pronounced temporal and spectral differences: The cyclisation proceeds with a characteristic time of $\sim$ 400 fs whereas the cycloreversion is about six times slower. Further, the transient fluorescence spectra of the photo-excited isomers significantly differ thoughout the reaction. We discuss the possible involvement of other excited states and a two-dimensional model to account for our observations.

MO 22: Cold Molecules I (gemeinsam mit Q)

Zeit: Dienstag 10:30–12:45 Raum: 6B

Hauptvortrag MO 22.1 Di 10:30 6B

Ultracold Molecular Ions in Radiofrequency Traps - Production and Spectroscopy — •Bernhard Roth, Jeroen Koelemeij, Chaobo Zhang, David Offenberg, Andreas Wicht, Ingo Ernsting, and Stephan Schiller — Institut für Experimentalphysik, Universitätsstr. 1, D-40225 Düsseldorf

A general method for the production of translationally cold charged molecules is sympathetic cooling by laser-cooled atomic ions. Recently, we have shown that using two coolant species only (beryllium and barium ions) molecular ions with masses from 2 to 470 amu can be cooled to temperatures of 10-100 mK. The wide range of coolable species makes the method attractive for many studies in chemical physics, molecular physics, fundamental physics, and astrochemistry. Since the molecular ions can be trapped for times exceeding minutes in a near-collision-less environment, light-molecule and molecule-molecule interactions in a new regime can be studied. Examples are precise spectroscopy, molecular quantum state preparation, internal coherence, interactions with neutral particles, spontaneous emission. In this talk we will describe preparation methods, spectroscopy results and outline future developments.

MO 22.2 Di 11:00 6B

Chemical Probing Spektroskopie von H_3^+ in einer kryogenen RF-Falle — •Max Berg, Annemieke Petrignani, Dennis Bing, Andreas Wolf und Holger Kreckel — Max-Planck-Institut für Kernphysik, Saupfercheckweg 1, 69117 Heidelberg

Das H_3^+ Molekülion spielt eine fundamentale Rolle in der Chemie des interstellaren Mediums, insbesondere für das Reaktionsnetzwerk in kalten Molekülwolken. Um aussagekräftige Messungen bei niedrigen Temperaturen (10-100 K) zu machen muss H_3^+ aktiv gekühlt werden, da wegen des fehlenden Dipolmoments die radiative Kühlung zu ineffektiv ist. Zu diesem Zweck wurde am Speicherring TSR eine 22-Pol Injektor-Falle entwickelt in der H_3^+ Ionen durch Stösse mit Helium Puffergas auf interstellare Temperaturen gekühlt werden können. Um die Population in den niedrigsten Rotationszuständen von H_3^+ nachzuweisen wird eine Chemical Probing Spektroskopie eingesetzt deren gesteigerte Sensitivität Messungen mit wenigen hundert Ionen ermöglicht. Besonderes Augenmerk wird dabei auf den Kernspin von H_3^+ gelegt und es wird gezeigt, dass die Nutzung von para-H_2 Gas eine Manipulation des ortho/para-Verhältnisses von H_3^+ erlaubt.

MO 22.3 Di 11:15 6B

A negative ion proton transfer reaction at extremely low temperatures — •Rico Otto, Jochen Mikosch, Sebastian Trippel, Christoph Eichhorn, Markus Debatin, Matthias Weidemüller, and Roland Wester — Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg

Using a low-temperature 22-pole ion trap we have studied the reaction of NH_2^- with molecular hydrogen in the temperature interval from 300 down to 8 Kelvin. We access in this experiment the, for negative ions previously unexplored, temperature regime below 25 Kelvin. For NH_2^- + H_2 we observe an unexpected decrease of the reaction rate coefficient at low temperatures, which is indicative of a very small reaction barrier. In this presentation we will present the new low-temperature 22-pole trap setup, the employed experimental scheme to obtain absolute reaction rate coefficients, and the measurements for the proton transfer from H_2 to NH_2^-. We will then discuss the current status of the interpretation of the measured rate coefficient. In future experiments we will investigate in how far the temperature dependence of the studied proton-transfer reaction represents a general behaviour of negative ion reactions at low temperature.

MO 22.4 Di 11:30 6B

Photodetachment of cold OH^- in a multipole ion trap — •Sebastian Trippel, Jochen Mikosch, Raphael Berhane, Rico Otto, Matthias Weidemüller, and Roland Wester — Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg

Negative ion photodetachment is the basis of many photoelectron spectroscopy studies. It is also a fundamental destruction process for negative ions in the environment. We have developed a method to deterimine the absolute photodetachment cross section of negative ions using a 22-pole radiofrequency ion trap. Previous studies have shown that these traps are well suited for collisional cooling of molecular vibrational and rotational states. In this work we present results for the photodetachment of trapped OH^- ions at 170 K rotational temperature. We obtain the absolute cross section in a direct and model-independent approach by measuring the decay constant of the trapped ions due to photodetachment. The density of ions interacting with the laser is measured in a tomography scan through the trap. In comparison with previous results, the cross section shows a sensitive dependence on the initial rotational state distribution. These results indicate that the rotational state dependence of the cross section is given by $(2J + 1)$, where J is the rotational quantum number of OH^-. This rotational-state dependence might be relevant for models of the abundance of negative ions in the atmosphere or in interstellar space.

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

MO 22.5 Di 11:45 6B

Production of Cold Neutral Molecules via the Deceleration and Photodetachment of Anions — •Andreas Osterwalder, Thomas Middelmann, and Gerard Meijer — Fritz-Haber-Institut der MPG, 14195 Berlin

A new method for the production of cold neutral molecules is presented: the molecules are prepared as negative ions, decelerated, and subsequently neutralized by photodetachment.

The neutrals shall be investigated by high-resolution spectroscopy and used for chemical dynamics research in the range below 10 K. Experiments in this temperature range are essential for a complete understanding of astrochemistry and of many fundamental aspects of scattering dynamics. Nevertheless, no experimental data are available.

The new approach has the following advantages over existing techniques:

1. It is very general since it can be applied to any neutral molecule that possesses a stable anion (which is the case for many molecules, ranging from small diatomics to large bio molecules);

2. A single species can be selected for the deceleration by coupling a mass-spectrometer to the deceleration apparatus;

3. Because the neutral is formed only at the very end of the deceleration procedure the technique is also well-suited for short-lived and reactive species (in particular also for radicals);

4. The choice of the detachment wave length allows the production of the neutral in the ground state or in an excited state.

MO 22.6 Di 12:00 6B

A molecular synchrotron — •Cynthia E. Heiner[1], David Carty[1], Hendrick L. Bethlem[1,2], and Gerard Meijer[1] — [1]Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany — [2]Laser Centre Vrije Universiteit, Amsterdam, The Netherlands

The tools for manipulating the motion of neutral atoms and molecules are inspired from the techniques developed for charged particles. Traps for atoms, akin to the Paul trap for ions, are widely implemented; surprisingly however, little attention has been paid to developing a neutral analog of a synchrotron. One great advantage of a synchrotron over a trap is that (many) bunches of cold molecules can be made to interact repeatedly, at well defined times and distinct positions with electromagnetic field and/or particles.

I will present recent results demonstrating a molecular synchrotron consisting of two hexapoles bent into a semi-circle separated by a 2 mm gap. I will detail our simple scheme for exploiting the fringe fields in these gaps to accelerate, decelerate, and focus along the longitudinal direction ("bunch") a packet of ammonia molecules. The stored bunch of cold molecules (T=0.5 mK) is confined to a 3 mm packet even after completing 40 roundtrips, which corresponds to a flight distance of over 30 meters. Furthermore, the injection of multiple packets into the ring will be shown.

MO 22.7 Di 12:15 6B

Efficient Cooling in Supersonic Jet Expansions of Supercritical Fluids — •Wolfgang Christen[1], Klaus Rademann[1], and Uzi Even[2] — [1]Institut für Chemie, Humboldt-Universität zu Berlin, Brook-Taylor-Strasse 2, 12489 Berlin, Germany — [2]Sackler School of Chemistry, Tel Aviv University, 69978 Tel Aviv, Israel

Pulsed, supersonic beams of carbon monoxide and carbon dioxide at stagnation conditions above their critical point have been investigated by time-of-flight measurements as a function of pressure and temperature[1]. Surprisingly large speed ratios (above 100) have been achieved that are indicative of very low translational temperatures ($\leq$ 0.1 K). In particular, the supersonic expansion of CO_2 at stagnation temperatures slightly above the phase transition to the supercritical state results in unprecedented cold beams. This efficient cooling is attributed to the large values of the heat capacity ratio of supercritical fluids in close vicinity of their critical point.

[1] Wolfgang Christen, Klaus Rademann, Uzi Even, *J. Chem. Phys.* **125**, 174307 (2006).

MO 22.8 Di 12:30 6B

Beams of slow and heavy molecules for interferometry — •András Major, Hendrik Ulbricht, Sarayut Deachapunya, and Markus Arndt — Fakultät für Physik, Universität Wien, Boltzmanngasse 5, A-1090 Wien

We show experimentally that an effusive source can create a slow beam of large molecules. Owing to the very slow speeds achieved with these molecules, whose molecular weights are comparable to that of insulin, this source promises exciting new possibilities in interferometry as well as the cooling and trapping of these molecules. This report also presents a theoretical evaluation of the results with the emphasis on supersonic expansion of the beam.

MO 23: Gustav-Hertz-Preis (Preisträgervortrag, gemeinsam mit K)

Zeit: Dienstag 14:00–14:30 Raum: 6C

Preisträgervortrag MO 23.1 Di 14:00 6C

Bewegte Bilder auf atomarer Längen- und Zeitskala: Femtosekunden Röntgenbeugung — •Matias Bargheer — Institut für Physik, Universität Potsdam, Am Neuen Palais 10, 14669 Potsdam — Max-Born-Institut, Max-Born-Str. 2a, 12489 Berlin

Femtosekunden-Röntgenbeugung (fs-XRD) kombiniert die strukturelle Auflösung der Röntgenbeugung (ca. 100 Femtometer) mit der Zeitauflösung der Pump-Probe Technik (ca. 100 Femtosekunden (fs)). Damit kann Dynamik in vielen physikalischen Systemen von Molekülen über weiche Materie bis hin zu Festkörpern auf atomarer Längen- und Zeitskala exakt vermessen werden. Anhand zweier Beispielexperimente wird gezeigt, wie man aus der genauen Beobachtung der Bewegung von Atomkernen entscheidende Rückschlüsse auf die mikroskopisch wirkenden Mechanismen ziehen kann. Insbesondere lässt sich so der dominante Mechanismus zur optischen Anregung kohärenter Phononen in Halbleiter-Übergittern rekonstruieren. Die Anregung von Elektronen im Halbleiter führt instantan zu einem verschobenen Gleichgewicht der parabolischen Potentiale für die Schwingungen der Kerne und ist somit analog zu einer Wellenpaketsbewegung nach einer vibronischen Anregung von Molekülen. Im zweiten Experiment wird die komplexe Funktion eines ferroelektrisch-metallischen Nanoschichtsystems aufgeklärt. Die optische Anregung erzeugt innerhalb von 500 fs einen Druck von 1 GPa, der über die anharmonische Kopplung zweier Schwingungsmoden zum Ausschalten der ferroelektrischen Polarisation nach 2000 fs führt.

MO 24: Femtosecond Spectroscopy III

Zeit: Dienstag 14:30–16:15 Raum: 6C

MO 24.1 Di 14:30 6C

Transient states and kinetics in the photochromic reaction of spironaphtoxazine — •Uwe Megerle, Uli Schmidhammer, Stefan Lochbrunner, and Eberhard Riedle — Lehrstuhl für BioMolekulare Optik, LMU München

We investigated the primary photoproducts of the photochromic molecular switch spironaphtoxazine (SNO) dissolved in DMSO. The experiments were performed by UV-excitation (345 nm) transient absorption spectroscopy with a time resolution of about 100 fs. The broad spectrum of the probe-continuum (350-750 nm) allowed observing the spectral characteristics of all intermediate states. By measuring kinetic curves at numerous wavelengths we determined precise rate constants for the different steps of the photoreaction. This was supported by examining the time dependence of the absorption shift as well as the temporal increase of the transition dipole moment. The relatively high viscosity and slow relaxation times of DMSO decelerate the isomerisation step in the ring opening reaction compared to other solvents and therefore facilitate the assignment of the observed decay times. Thus the sequence of processes on both potential energy surfaces becomes much clearer than in cyclohexane and acetonitrile solutions that were investigated for comparison and can be directly compared to recent calculations [1].

[1] F. Maurel, J. Aubard, P. Millie, J.P. Dognon, M. Rajzmann, R. Guglielmetti and A. Samat, J. Phys. Chem. **110** (2006), 4759.

MO 24.2 Di 14:45 6C

Dual Fluorescence in the Photochemical ZE Isomerization of Hemistilbene/Hemithioindigo-Molecules (HTI) — •Thorben Cordes[1], Nadja Regner[1], Björn Heinz[1], Tobias Schrader[1], Christian Hoppmann[2], Karola Rück-Braun[2], and Wolfgang Zinth[1] — [1]LMU München, Lehrstuhl für BioMolekulare Optik, Oettingenstraße 67, 80538 München — [2]Technische Universität Berlin, Institut für Chemie, Straße des 17. Juni 135, 10623 Berlin

Photoinduced isomerizations are intensively studied reactions due to their importance in chemistry and biology. Systems containing conjugated double bonds (e.g. stilbene, hexatriene) are used as model systems for Rhodopsin or Carotinoids to investigate ultrafast photoreactions and to understand them in detail. A combination of a hemistilbene part with the half of a thioindigo-dye brings up a new class of photochromic compounds. It could be shown, that these HTI-molecules are suitable to act as ultrafast light trigger in chromopeptides[1]. In this context these photoinduced reactions have been studied with pump-probe spectroscopy in the visible. To obtain a clear insight in the photochemical pathway the transient absorption data is complemented with time-resolved fluorescence and IR measurements. By combination of these techniques the photochemical pathway of the ZE isomerization is revealed.

[1] T. Cordes et. al. Chem. Phys. Lett. 428 (2006) 167-173

MO 24.3 Di 15:00 6C

Einfluss von Substitution und Umgebungsvariablen auf die photoinduzierte Isomerisierung von Hemistilben/Hemitioindigo-Molekülen — •Markus Lipp[1], Thorben Cordes[1], Torsten Schadendorf[2], Karola Rück-Braun[2] und Wolfgang Zinth[1] — [1]LMU München, Lehrstuhl für BioMolekulare Optik, Oettingenstraße 67, 80538 München — [2]Technische Universität Berlin, Institut für Chemie, Straße des 17. Juni 135, 10623 Berlin

Hemistilbene/Hemithioindigo-Moleküle zeigen interessante photochrome Eigenschaften. Durch Licht im sichtbaren/UV Spektralbereich kann ultraschnell (ps - ns) zwischen zwei isomeren Zuständen (Z/E) geschaltet werden. Reaktionsgeschwindigkeit sowie Reaktions- und Fluoreszenzquantenausbeute hängen stark von der Substitution des Hemistilbenteils ab. Allgemein läuft die ZE Reaktion langsamer als die EZ Richtung ab, weiterhin ist ein Einfluss von Umgebungsvariablen wie Lösungsmittel und Temperatur auf alle genannten Parameter beobachtbar. Die qualitative Beschreibung dieses Verhalten durch Barrieren auf der Potentialfläche des angeregten Zustandes werden durch temperaturabhängige Messungen untermauert. Die Beobachtungen werden in ein Modell für die photochemische Umwandlung der beiden isomeren Zustände eingebracht und stützen das entwickelte Modell.

MO 24.4 Di 15:15 6C

Zeitaufgelöste akkumulative Spektroskopie einer Photoreaktion — •Florian Langhojer[1], Frank Dimler[1], Gregor Jung[2] und Tobias Brixner[1] — [1]Physikalisches Institut, Universität Würzburg, Am Hubland, 97074 Würzburg — [2]Biophysikalische Chemie, Universität des Saarlandes, 66123 Saarbrücken

Bei bisher üblichen Techniken für femtosekundenaufgelöste Experimente werden gleiche Ausgangsbedingungen für jeden neuen Laserimpuls hergestellt, indem jede Wechselwirkung mit einem neuen Probenvolumen stattfindet. Wir präsentieren das Konzept und Anwendungen der akkumulativen Detektion von Photoprodukten. Ein solcher Aufbau erlaubt die Wechselwirkung vieler identischer Laserpulse bzw. Pulsfolgen mit einem kleinen Flüssigkeitsvolumen. Nach einer gewissen Zeit werden die akkumulierten, stabilen Photoprodukte detektiert. So können auch Photoreaktionen mit geringen Produktausbeuten beobachtet werden, deren Messsignal für konventionelle Spektroskopie zu gering wäre. Das Probenvolumen wird dann automatisiert ausgetauscht und das Experiment kann mit anderen Laserimpulsen bzw. unterschiedlichen Pump-Probe-Verzögerungszeiten wiederholt werden.

Der Akkumulationsprozess wird quantitativ betrachtet. Die Methode wurde auf die Photokonversion des Grün Fluoreszierenden Proteins (GFP) angewandt. Nach der Anregung mit einem Laserimpuls um 400 nm kann durch Absorption eines 800 nm Photons eine Photoreaktion mit stabilem Produkt erfolgen. Wir haben die Zeitabhängigkeit dieser Reaktion untersucht.

MO 24.5 Di 15:30 6C

Early excited state dynamics of β carotene near a conical intersection detected by Pump – Degenerate Four Wave Mixing (Pump – DFWM) — •Jürgen Hauer, Tiago Buckup, and Marcus Motzkus — Physikalische Chemie, Philipps-Universität Marburg, D-35032 Marburg, Germany

The early femtosecond dynamics on the electronically excited states of carotenoids play a crucial role in photosynthetic light harvesting. For understanding the evolution of β carotene near the conical intersection between its first two excited states, it is necessary to study the interplay between electronic and nuclear dynamics. We use a time domain method (Pump – DFWM [1]) yielding both time resolved excited state molecular Raman modes and information on the development of the involved electronic states.

Degenerate Four Wave Mixing (DFWM) has already proven to be a versatile tool for studying and controlling vibrational dynamics on β carotene's ground state. [2]. Introducing an additional pump pulse preceding the DFWM – sequence, allows studying excited state vibrations. The technique delivers a time resolution only limited by the duration of the employed ultrashort pulses (sub 20 fs) and a spectral resolution better than 20 cm^{-1}.

Since the DFWM - signal shows a decay time constant depending on the electronic state under investigation, the experiment also yields results on population dynamics near the conical intersection.

[1] Hornung et al., Chemical Physics Letters 402 (2005) 283–288
[2] Hauer et. al., Chemical Physics Letters 421 (2006) 523–528

MO 24.6 Di 15:45 6C

Model studies of laser induced femtosecond dynamics in the excited states of β-carotene — •Judith Voll, Benjamin Fingerhut, and Regina de Vivie-Riedle — LMU Department Chemie, Butenandt-Str. 11, 81377 München, Germany

Based on data from coherent control experiments performed on β-carotene in the group of M. Motzkus we present a model for the theoretical description of the laser induced quantum dynamics. After excitation by a femtosecond pulse from the electronic ground state into the S_2 state the system relaxes via conical intersections and is then detected in the S_1 state by transient raman spectroscopy.

To specify the kinetic hamiltonian, the raman modes involved, their force constants and the relative position of the interacting potentials were extracted from ab initio calculations. With this model the mechanism of internal conversion is studied, incorporating vibrational cooling in the S_1 state. The influence of the topology of the electronic states as well as the position of the S_2 - S_1 conical intersection on the dynamics are examined. These results are used to investigate the controllability of the transfer rate by modulated laser pulses.

MO 24.7 Di 16:00 6C

Femtosecond Optical and Vibrational Spectroscopy: Evidence for Vibronic Coupling — •Alexander Weigel, Alexander Dobryakov, and Luis Perez Lustres — Humboldt Universität zu Berlin, Fachbereich Chemie, Brook-Taylor-Str. 2, 12489 Berlin

Flavin derivatives serve as antenna pigments in blue light photoreceptors. To gain insight into primary activation steps the dynamics of riboflavin in solution was examined by ultrafast transient absorption spectroscopy. After vibrationless S_1 excitation at 490 nm the signal rises on the timescale of solvation dynamics and decays in agreement with the fluorescence lifetime. The transient spectra shape exhibits a significant solvent dependence. In aprotic DMSO environment stimulated emission and ground state bleach are of similar intensity, whereas in protic aqueous solution the stimulated emission band is diminished already at time zero indicating strong coupling to nearby dark states.

Excitation with 5000 cm^{-1} excess of energy evidences vibronic coupling in DMSO as well. Most strikingly, the transient spectrum evolves non-exponentially and shows strong oscillation with a frequency of 95 cm^{-1}. The quantum dynamics could be modelled by assuming a degenerate two state system with complete population of the S_1 state at time zero while damping occurs through intramolecular vibrational redistribution of S_1.

The results were further supported by femtosecond stimulated Raman experiments.

MO 25: Cold Molecules II (gemeinsam mit Q)

Zeit: Dienstag 14:00–16:15 Raum: 6B

Hauptvortrag MO 25.1 Di 14:00 6B

Manipulating large molecules: selecting isomers, orienting, and slowing polar molecules with strong electric fields — •Jochen Küpper — Fritz-Haber-Institut der MPG, Faradayweg 4-6, 14195 Berlin

Polar molecules can be manipulated using strong electric fields. Small molecules, for example OH or NH_3, have been focused and state selected by electrostatic multipole guides, they have been slowed in Stark decelerators and stored in rings or traps. Practically all these experiments have been performed on molecules in low-field-seeking quantum states. For larger molecules, however, all states are high-field seeking at the relevant electric field strengths.

To manipulate the motion of large molecules one has to use Alternate Gradient (dynamic) focusing. In prototype experiments small molecules in high-field seeking states have been decelerated [1]. We are extending these methods to the focusing and deceleration of large molecules. For large (bio-)molecules typically a number of different conformers (structural isomers) are present in a supersonic jet. Using switched electric fields in a "quadrupole" guide such conformers can spatially be separated due to their different mass-to-dipole (m/μ) ratios, similar to a quadrupole mass-to-charge (m/q) filter for ions. Moreover, the molecular packets transmitted through the guide are very well suited for brute-force orientation.

We have also set up a modular Alternate Gradient deceleration experiment, which allows us to slow polar molecules in low- and high-field seeking states. We have successfully decelerated several molecules, for example benzonitrile (C_7H_5N), in different quantum states.

I will discuss the prospects for novel studies on such molecular systems that these experiments on the structural and spatial separation and the deceleration of large molecules offer. For example, oriented samples of individual conformers of large molecules will greatly benefit scattering experiments for direct structure determination.

[1] H. L. Bethlem, M. Tarbutt, J. Küpper, D. Carty, K. Wohlfart, E. Hinds, and G. Meijer, *J. Phys.* B **39**, R263 (2006)

MO 25.2 Di 14:30 6B

Molecular fine structure of strong dipolar molecules — •J. Deiglmayr, M. Aymar, and O. Dulieu — Laboratoire Aimé Cotton, CNRS, Bâtiment 505, Campus d'Orsay, 91405 Orsay Cedex, France

Recently the production of ultracold heteronuclear molecules in their electronic ground state either via photoassociation [1] or Feshbach resonances [2] has been achieved. Such heteronuclear molecules, if deeply bound, have a significant permanent electric dipole moment leading to strong, long-range, and alignment dependent intermolecular forces, which offer control by external electromagnetic fields. We have calculated the R-dependent polarizabilities for all heteronuclear dimers in the ground state using quantum chemistry methods [3]. We also follow a new approach to include spin-orbit coupling in ab-initio calculations of molecular potentials: a full configuration interaction calculation with effective core potentials and a diabatization procedure is used to determine potential curves with fine structure. These new insights will be used to find efficient routes to produce and stabilize polar molecules, to model the dynamics of a dipolar gas in an optical dipole trap and to explore external field dependent scattering properties.

[1] A Kerman *et al.*, PRL 92 (2004) 153001; D Wang *et al.*, PRL 93 (2004) 243005; MW Mancini *et al.*, PRL 92 (2004) 133203; C Haimberger *et al.*, PRA 70 (2004) 021402(R); SD Kraft *et al.*, J. Phys B 39 (2006) S993
[2] C. Ospelkaus *et al*, PRL 97 (2006) 120402
[3] M. Aymar, O. Dulieu, J.Chem.Phys 122 (2005) 204302

MO 25.3 Di 14:45 6B

Electrostatic extraction of buffer-gas-cooled polar molecules — •Laurens D. van Buuren, Joseph Bayerl, Vincent Dugrain, Sebastian Pohle, Christian Sommer, Pepijn W.H. Pinkse, and Gerhard Rempe — Max-Planck-Institut für Quantenoptik, Hans-Kopfermann-Str. 1, 85748 Garching, Germany

High-density samples of cold molecules are required to investigate their collisional and chemical properties at low temperatures. Once polar molecules can be cooled to the ultracold regime, where the dipole-dipole interaction dominates, new quantum phenomena can be studied. Cold polar molecules are also of interest for high-resolution spectroscopy, metrology, and quantum computation [1].

We present first results with a new cryogenic source delivering a dense and slow beam of internally cold molecules. The beam is produced by combining two powerful techniques. Molecules are cooled (translationally and internally) in a helium buffer gas at low temperature (T $\sim$ 5 K) [3]. With an electric guide slow buffer-gas-cooled molecules are filtered out of the (non-polar) helium and transported to a high-vacuum region [2], where the flux is analysed. Once the source is optimized, the cold molecules can easily be loaded into an electrostatic trap [4] for further investigations.

[1] J. Doyle et al., European Physical Journal D **31**, 149 (2004)
[2] T. Junglen et al., European Physical Journal D **31**, 365 (2004)
[3] S.E. Maxwell et al., Physical Review Letters **95**, 173201 (2005)
[4] T. Rieger et al., Physical Review Letters **95**, 173002 (2005)

MO 25.4 Di 15:00 6B

Cavity Cooling of internal and external degrees of freedom of molecules. — •Giovanna Morigi[1], Pepijn Pinkse[2], Markus Kowalewski[3], and Regina de Vivie-Riedle[3] — [1]Departament de Fisica, Universitat Autonoma de Barcelona, E-08193 Bellaterra, Spain — [2]Max-Planck-Institut für Quantenoptik, Hans-Kopfermann-Str. 1, 85748 Garching — [3]LMU Department Chemie, Butenandt-Str. 11, 81377 München

A proposal is presented for effectively cooling vibrational, rotational, and translational degrees of freedom of molecules. The molecules are driven by off-resonant laser light and cooled through Raman processes, where photons are scattered into the resonator, which then decays into free space. Photon emission occurs at a multitude of cavity resonances in a suitably designed resonator. The cooling efficiency is investigated numerically for the case of the OH radical, using ab-initio data and taking into account the rovibrational dependence of the Raman scattering into the cavity modes. Extentions to more complex molecules will be considered.

MO 25.5 Di 15:15 6B

Alternate Gradient deceleration of large molecules — •Kirstin Wohlfart, Frank Filsinger, Jochen Küpper, and Gerard Meijer — Fritz-Haber-Institut der MPG, Faradayweg 4–6, 14195 Berlin

Over the last years fascinating progress has been made in the spectroscopy of large (bio-)molecules, e.g. the *building blocks of life*. Meanwhile, our group has been developing methods to decelerate and cool neutral, polar molecules using time varying electric fields. In order to extend these techniques to the deceleration of large or heavy molecules, which have practically only high-field seeking states, or molecules in their absolute ground state, Alternate Gradient focusing must be applied. We showed that this technique can be used to focus and decelerate molecules in high-field seeking states [1].

Using a modular Alternate Gradient deceleration experiment different states of benzonitrile (C_7H_5N) and OH, in both high-field and low-field seeking components of its ground state, have been decelerated. The time-of-flight profiles are quantum-state-selectively measured using high-resolution laser induced fluorescence spectroscopy. We compare the efficiency of different high voltage switching schemes and will discuss the prospects of future experiments for the deceleration of larger molecules.

[1] H. L. Bethlem, M. Tarbutt, J. Küpper, D. Carty, K. Wohlfart, E. Hinds, and G. Meijer, *J. Phys. B* **39**, R 263 (2006)

MO 25.6 Di 15:30 6B

Supersonic Beams at High Stagnation Pressures: Thermodynamics and Translational Cooling — •Wolfgang Christen, Tim Krause, Sibylle Rabeus, and Klaus Rademann — Institut für Chemie, Humboldt-Universität zu Berlin, Brook-Taylor-Strasse 2, 12489 Berlin, Germany

Pulsed, supersonic beams of rare gases at high stagnation pressures ($10 < p_0 < 120$ bar) have been investigated by time-of-flight measurements as a function of gas temperature T_0. The numerical evaluation of the arrival time distribution $f(t)dt$ permits an accurate determination of the velocity distribution, characterized by the flow velocity v_0 and the velocity spread $\Delta v_{\|}$ of the expanded beam. We compare the

experimental results $v_0(p_0, T_0)$ with values calculated for a supersonic expansion of an ideal gas. Because the translational cooling of a supersonic jet is usually characterized by the speed ratio $S = v_0/\Delta v_\parallel$, we discuss the applicability of this approach at high pressure conditions. The effect of condensation on cooling is investigated by retarding field measurements, determining the cluster size distribution in the beam.

MO 25.7 Di 15:45 6B

Deceleration of polar molecules using a microstructured electrode array — •Samuel Meek, Hendrick Bethlem, Horst Conrad, and Gerard Meijer — Fritz-Haber-Institut der MPG, Faradayweg 4-6, 14195 Berlin

By utilizing the forces that polar molecules experience in inhomogenous electric fields, a variety of molecular-optical elements have been experimentally demonstrated. While previous electrode configurations at the mm scale require potential differences of tens of kV at the electrodes, similar fields can be produced between $10\mu m$-sized electrodes using potentials of hundreds of volts. Here, we present trajectory calculations for a recently constructed electrostatic decelerating and trapping device consisting of a periodic array of 1254 microstructured linear electrodes deposited on a planar glass substrate. Application of harmonic waveforms to periodic groups of six electrodes forms a series of periodic minima which move along the array in a continuous manner without changing their distances above the electrodes. Deceleration is achieved by linearly reducing the frequency of the applied waveforms.

First experiments have already been performed using beams of $a^3\Pi_1$ CO, which has a lifetime of a few milliseconds. Such a long lifetime allows laser excitation directly after the nozzle where the densities are higher, followed by detection of the fluorescence with a photomultiplier tube, or using Auger deexcitation at a microchannel plate or a gold surface. Operating the device in a mirror mode by applying a static dipole field, we were able to vary the deflection of the molecules from one to four degrees, simply by changing the tilt of the structure.

MO 25.8 Di 16:00 6B

Trapping ground-state molecules — •Melanie Schnell, Jacqueline van Veldhoven, Peter Lützow, Bretislav Friedrich, Hendrick Bethlem, and Gerard Meijer — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin

Trapping of neutral molecules in high-field seeking states is important since the absolute molecular ground state and most of the states of heavier molecules with small rotational constants are high-field seeking. When molecules are trapped in their absolute ground state with a high enough density and the trap depth can be varied, increasing their phase-space density via evaporative cooling will be possible, as trap loss due to inelastic collisions can be avoided. This is one important step towards the realization of a molecular Bose-Einstein condensate. Another application is located in the field of high-resolution spectroscopy. Due to the long interaction times of the trapped molecules with the electromagnetic radiation an increased resolution in the spectroscopic experiment can be reached.

Trapping ground state molecules, however, is challenging since the realization of a maximum of a static electric field in free space is not possible. It can be achieved using time-dependent fields. One approach is to employ dynamic confinement using switched electric fields (AC trap). So far, both a cylindrically symmetric and a linear AC trap have been realized. We will present our newest results on AC trapping, which include the characterization of the two traps, and we will discuss some future applications of AC trapping of ground state molecules.

MO 26: Poster: Biomolecules

Zeit: Dienstag 16:30–18:30 Raum: Poster A

MO 26.1 Di 16:30 Poster A

Saturation Threshold of Adsorption Reaction of Lysozyme on Surfaces of Nanodiamond/Nanosilica — •Victor Wei-Keh Wu — Department of Chemical and Material Engineering, National Kaohsiung University of Applied Sciences, 80782 Kaohsiung, Taiwan — Group 510, Institute of Atomic and Molecular Sciences, Academia Sinica, P.O.Box 23-166, 10617 Taipei, Taiwan — Victor Basic Research Laboratory e. V. Gadderbaumer-Str. 22, 33602 Bielefeld, Germany, Email:victorbres3tw@yahoo.com.tw, http://www.che.kuas.edu.tw

Fluorescences from free lysozyme of 0-1000 nM in 7 mM PPBS at pH = 11.0 after adsorption reactions on the surfaces of nanodiamond (100 nm, No.I-21, carboxylated; KDM, Kay Diamond) and nanosilica (100 nm, VP OX 10, degussa) with Xe lamp as light source monochromated (Tandem GM252, ABI Analytical) at 285 nm of ca. 0.6 mW and PMA-11 of Hamamatsu as fluorescence spectrometer have been measured. Each of 2 mL lysozyme solutions was treated with 50 μg suspension of nanodiamond/-silica in 20 μL PPBS. BET and Langmuir surface areas, 55 and 80 m^2/g for nanodiamond, 15 and 20 m^2/g for nanosilica, respectively, have been obtained by use of adsorptive dose rate, and static volumetric measurement technique, where BET surfaces are applicable. Saturation thresholds of adsorption of lysozyme have been measured at 190 and 175 nM; 110 and 101 mg lysozyme adsorbed for 1 g nanodiamond/-silica can be estimated, respectively. The adsorbed lysozyme on an unit surface of nanoparticle can finally be obtained as 2.0 and 1.8 [mg-lysozyme/m^2-nanoparticle] for nanodiamond/-silica, respectively. **Ref.** V. W.-K. Wu, Chem. Lett. 35, 1380 (2006).

MO 26.2 Di 16:30 Poster A

Screening Biological Systems by Raman Scattering Techniques — Towards Specific Characterization of Tumors on a Molecular Level — •Patrice Donfack, Malte Sackmann, and Arnulf Materny — International University Bremen IUB (Jacobs University Bremen as of Spring 2007), Germany

Cancer is a severe disease connected with progressive radical molecular distortions in the host cells. Since many years vibrational Raman spectroscopy (RS) and related techniques have been recognized as powerful tools for probing molecular vibrations giving rise to molecular fingerprints. In a non-destructive and non-invasive way even relatively small molecular distortions can be detected. An early detection of the onset of biological deterioration is possible only if specific molecular information can be obtained that becomes distinguishable as soon as changes occur. Understanding molecular events in biological systems at molecular level appears would be an outstanding attainment allowing for a monitoring of the behavior of biological systems and the discrimination between healthy and cancerous states. Obviously, a potential approach would consist of a combination of many methods. We are applying spontaneous RS, surface enhanced Raman scattering (SERS) as well as biochemical molecular recognition techniques. Our goal is to differentiate and histopathologically assign spectroscopic changes that occur between healthy cells or tissue and to identify tumors in different stages of their development. Results obtained from RS and SERS applied to tissue sections and cells for different experimental environments and conditions are discussed.

MO 26.3 Di 16:30 Poster A

Revealing Food Quality by Raman Spectroscopy — •Rasha Hassanein, Patrice Donfack, Malte Sackmann, and Arnulf Materny — International University Bremen (Jacobs University Bremen as of Spring 2007), Germany

In the food industry, various ingredients and biopolymers are commonly used in order to optimize the texture or the flavor of food. The distribution and the microstructure of the ingredients strongly determine the properties of the final product. Therefore, research and development as well as quality control require powerful analytical tools for studying the distribution of the various compounds.

Raman spectroscopy provides a nondestructive method to determine the chemical composition of a sample and requires only a minimum of sample preparation. Raman spectroscopy has therefore become a widely used technique for analytical purposes both in industry and scientific research. However, up to now only little work was invested in an application of this spectroscopical method in food chemistry. In our recent work, we have started to investigate food quality applying various Raman techniques. Because food quality is very often mainly determined by ingredients, which may be present at low concentrations or which are trapped in a complex matrix, separation methods have to be improved and an enhancement of the Raman signal is required. For the latter, surface enhanced Raman scattering is used, which also helps to suppress the fluorescence background. In our contribution, we

discuss our first experiments, which *e.g.* aimed at the characterization of different types of whisky.

MO 26.4 Di 16:30 Poster A

Femtosecond transient absorption studies on the photolyase of Thermus thermophilus and their chromophores FMN and FAD — Annette Brunsen, •Tiago Buckup, Tobias Klar, Lars-Oliver Essen, and Marcus Motzkus — Physikalische Chemie, Philipps Universität Marburg, D-35032 Marburg, Germany

CPD-photolyases are enzymes which use blue light to repair UV-induced DNA damage. Flavins, like FAD and FMN, are the corresponding enzyme cofactors responsible for light absorption and the first step in the DNA repair reaction. In spite of the importance of photolyase in nature, very little is known about the ultrafast dynamics after the initial light absorption. In this work we investigate the mutant CPD-photolyase of Thermus thermophilus, which contains FAD only, with femtosecond transient absorption. The dynamics of the mutant photolyase is compared to the transient absorption signal of isolated FAD and FMN in different solvents. After excitation at 450 nm, ground-state bleach, excited-state absorption and stimulated emission could be measured between 450-900 nm. A fast solvent dependent time constant (2-10 ps) was observed and related to the closed form of FAD and dimerisation of FMN. Another long time constant is associated with the open and non-dimerised form. The transients of a mutated photolyase can be compared to those of FAD in water.

MO 27: Poster: Collisions and Energy Transfer

Zeit: Dienstag 16:30–18:30 Raum: Poster A

MO 27.1 Di 16:30 Poster A

Dekohärenz molekularer Konfigurationszustände — •Johannes Trost und Klaus Hornberger — Arnold Sommerfeld Center for Theoretical Physics, LMU München

Superpositionszustände von Enantiomeren, d.h. von isomeren Molekülen mit unterschiedlicher Konfiguration, werden bei komplexeren Molekülen nicht beobachtet. Um zu beurteilen in wie weit die Kohärenz solcher quantenmechanischer Superpositionen durch Streuprozesse mit Umgebungsgasen beschränkt wird, entwickelten wir ein Modell für chirale Moleküle, das es erlaubt, die dispersive Wechselwirkung konsistent und realistisch zu beschreiben. Anhand dieser chiralitätsabhängigen Wechselwirkungen lässt sich die Dekohärenzrate durch Gasstreuung streutheoretisch berechnen.

MO 27.2 Di 16:30 Poster A

Crossed-beam imaging of reactive scattering — •Christoph Eichhorn, Jochen Mikosch, Sebastian Trippel, Rico Otto, Markus Debatin, Matthias Weidemüller, and Roland Wester — Physikalisches Institut, Universität Freiburg, 79104 Freiburg

Among ion-molecule reactions, the nucleophilic substitution mechanism (S_N2) has gained attention because its quantum dynamics depend sensitively on the transition between entrance and exit channel complexes, which are seperated by a potential energy barrier [1]. Trajectory simulations [2] show e.g. that recrossing may lead to high internal excitation of the products.

We use crossed beam imaging in combination with sliced 3D velocity mapping, to study the differential cross section of the S_N2 reaction $Cl^- + CH_3I \longrightarrow CH_3Cl + I^-$ at relative collision energies between 0.7eV and 3eV. This allows us to measure the vibrational excitation of the CH_3Cl product molecule. While at low relative energy the reaction is dominated by strong backward scattering attributed to the S_N2 mechanism, much higher scattering angles are observed for higher collision energies, indicating a reaction without a collinear approach. Also an increase in the internal energy is observed.

Furthermore, we are developing the tools to study ion-molecule scattering with laser-aligned molecules [3], and laser assisted collisions.

[1] M.L.Chabinyc *et al.*, Science, **279**, 1882 (1998) [2] W.L.Hase, Science, **266**, 998 (1994) [3] H.Stapelfeldt and T.Seideman, Rev. Mod. Phys. **75**, 543 (2003)

MO 27.3 Di 16:30 Poster A

Elektronentransfer in ausgerichtete Wasserstoff-Molekülionen bei langsamen Stößen mit Helium — •Sven Schössler, Lothar Ph. H. Schmidt, Lutz Foucar, Horst Schmidt-Böcking und Reinhard Dörner — Institut für Kernphysik der J.W.Goethe Universität, Max-von-Laue-Str. 1, 60438 Frankfurt am Main, Deutschland

Bei Stoßgeschwindigkeiten unter 1 a.u. wurde der dissoziative Elektronentransfer bei der Reaktion $H_2^+ + He \rightarrow H_2^* + He^+ \rightarrow H + H + He^+$ untersucht. Das He^+ Rückstoßion wurde mit der COLTRIMS-Methode vermessen, koinzident dazu wurden die beiden neutralen Wasserstoff-Atome des Projektils auf einem ortsauflösenden multihitfähigen MCP-Detektor mit Delay-Line-Auslese detektiert.

Die kinematisch vollständige Messung erlaubt die Selektion des Reaktionskanals, bei dem die Molekülfragmente und das He^+ Target im elektronischen Grundzustand sind. Für diesen Kanal werden die Daten in inverser Kinematik präsentiert: Hier streut ein He-Atom an einem H_2^+ Molekül und gibt an dieses ein Elektron ab. Aus der Aufbruchrichtung des Moleküls kann die Orientierung beim Stoß bestimmt werden. Für die Reaktionen, bei denen das Molekül senkrecht zur Strahlrichtung gestanden hat, wird für das He-Ion ein Beugungsmuster beobachtet, das mit guter Nährung als Interferenz von zwei Kugelwellen beschrieben werden kann.

MO 28: Poster: Cluster

Zeit: Dienstag 16:30–18:30 Raum: Poster A

MO 28.1 Di 16:30 Poster A

Laserspektroskopie an negativ geladenen, massenselektierten Molekülen und Komplexen — •Michaela Entfellner, Martin Tschurl und Ulrich Boesl — TU München, Department Chemie, Physikalische Chemie 1, Lichtenbergstrasse 4, 85748 Garching, Deutschland

Die Methode der Anionen-Photodetachment-Photoelektronen-Spektroskopie (Anionen-PD-PES) ermöglicht an Molekülen und Molekül-Komplexen massenselektive Spektroskopie, insbesondere die Bestimmung von Elektronenaffinitäten. In unserer Apparatur steht am Anfang die Erzeugung von Anionen durch Anlagerung langsamer Elektronen. Nach der Massenselektion werden die zuvor angelagerten Elektronen mit einem festfrequenten Laser vom Molekül abgelöst (Photodetachment) und in einem Elektronen-Flugzeitspektrometer nachgewiesen. Eine weitere Methode stellt die Photodetachment-Spektroskopie (PDS) dar. Hier wird die Wellenlänge des eingestrahlten Lichts variiert und der totale Elektronen- oder Neutralenstrom gemessen. Man erhält so Informationen über den neutralen Zustand. Mittels IR-Dissoziationsspektroskopie erhält man schließlich die Schwingungsfrequenzen der anionischen Komplexe. Durch das Bestrahlen eines schwach gebundenen molekularen Komplexes mit IR-Laserlicht wird dieser zur Dissoziation gebracht. Durch Detektion der neutralen oder anionischen Fragmente wird so ein IR-Spektrum erhalten. Im präsentierten Poster werden neue molekulare Systeme vorgestellt, bei denen sich diese Kombination von spektroskopischen Methoden als sehr aufschlussreich erwies.

MO 29: Poster: Cold Molecules

Zeit: Dienstag 16:30–18:30 Raum: Poster A

MO 29.1 Di 16:30 Poster A

BEC in the Coffee Mug? — •Whally Dilbert — United Feature Syndicate, Inc.

During the recent years, unprecedented levels of unverifiable productivity were achieved with shaped sips. We will discuss slurping efficiency on a temperature scale from 350K down to a few mK. Predictions of the sippability of an eventually emerging BEC will be made.

MO 29.2 Di 16:30 Poster A

Controlling Molecular Orientation through Radiative Rotational Transitions in Strong Static Electric Fields — •Michael Mayle[1], Rosario Gonzalez-Ferez[2], and Peter Schmelcher[1,3] — [1]Theoretische Chemie, Physikalisch-Chemisches Institut, Im Neuenheimer Feld 229, D-69120 Heidelberg, Germany — [2]Instituto 'Carlos I' de Física Teórica y Computacional and Departamento de Física Atómica Molecular y Nuclear, Universidad de Granada, E-18071 Granada, Spain — [3]Physikalisches Institut, Universität Heidelberg, Philosophenweg 12, D-69120 Heidelberg, Germany

The effects of a static, homogeneous and strong electric field on the radiative and steric properties of the LiCs molecule in its $^1\Sigma^+$ electronic ground state are investigated. Combining discretization and basis-set methods, the rovibrational Schrödinger equation is solved and dipole transition rates are calculated. Spontaneous emission decay rates and radiative lifetimes of rovibrationally excited states have been studied extensively, incorporating in particular the interaction with the external field. Furthermore, the intriguing possibility to control the alignment and orientation of the molecules by applying a sufficiently strong field while switching between different rotational configurations via absorption and emission processes is demonstrated.

MO 29.3 Di 16:30 Poster A

Spectroscopy of the $X^1A_1 \rightarrow A^1A_2$ transition of formaldehyde in the 329-331.7 nm region: The $2_0^1 4_0^3$ rovibrational band — •Michael Motsch, Markus Schenk, Martin Zeppenfeld, Pepijn W.H. Pinkse, and Gerhard Rempe — Max-Planck-Institut für Quantenoptik, Hans-Kopfermann-Str. 1, 85748 Garching, Germany

Optical manipulation of cold polar molecules necessitates a molecule with strong electronic transitions, preferably in a spectral region accessible with standard cw-laser techniques, and a large Stark shift for efficient electric guiding and trapping. Slow beams of up to $10^{10}\,s^{-1}$ formaldehyde molecules with velocities around 50 m/s have been produced [1]. Moreover formaldehyde (H_2CO) exhibits a rich ultraviolet spectrum between 280 and 360 nm [2].

Room-temperature absorption spectroscopy is performed in a multipass setup at H_2CO pressures of 50 Pa. The use of a frequency-doubled cw dye laser allows higher resolution than previous studies relying on pulsed dye lasers [3]. Comparison between calculations based on available rotational constants and our measurement indicates the necessity to include sixth-order centrifugal distortion coefficients.

Progress towards state-dependent detection of electrically guided formaldehyde molecules is discussed.

[1] S.A. Rangwala et al., Phys. Rev. A **67**, 043406 (2003)
[2] G. Herzberg, Molecular Spectra and Molecular Structure 3, Van Nostrand Reinhold Company, New York 1966
[3] C.A. Smith et al., J. Phys. Chem. A **110**, 11645-11653 (2006)

MO 29.4 Di 16:30 Poster A

Interactions of negative ions in multipole traps — •Jochen Mikosch[1], Sebastian Trippel[1], Rico Otto[1], Markus Debatin[1], Michael Kröner[2], Christoph Eichhorn[1], Peter Woias[2], Matthias Weidemüller[1], and Roland Wester[1] — [1]Physikalisches Institut, Universität Freiburg — [2]Institut für Mikrosystemtechnik, Universität Freiburg

We study reactions of negative ions down to the previously unexplored temperature range below 25 Kelvin, where small molecular ions are prepared predominantly in the rovibrational ground state. Here we present recent results obtained in a temperature variable 22pole trap. Evaporation of atomic anions over the effective barrier gives insight into the stability of ion motion and allows us to determine absolute trap depths. The absolute cross section of OH^- photodetachment was measured using a tomography scan and found to depend on the rotational quantum state. Proton transfer from H_2 to NH_2^- shows an unexpected decrease in the absolute rate coefficient below 20 K indicating a very small reaction barrier. Finally, the three body association of Cl^- with CH_3Cl is strongly dependent on the internal structure of the stabilizing agent and shows a very strong enhancement for decreasing temperature.

In a new project we aim at interactions of trapped anions with ultracold Rubidium atoms. For this purpose we have developed a planar 32 pole ion trap on a chip; first storage results have been acchieved. The next ion trap generation will employ ITO electrodes with high optical transmission to allow laser cooling of atoms inside the ion trap.

MO 29.5 Di 16:30 Poster A

Trapping and cooling of single molecular ions for time resolved electron diffraction — •Günther Leschhorn, Steffen Kahra, Axel Friedenauer, Hector Schmitz, Ernst Fill, and Tobias Schätz — Max-Planck-Institut für Quantenoptik, Garching

We propose an experimental setup for the preparation of single, cold and localized molecular ions using a linear Paul-trap. The ions are cooled sympathetically by a Mg^+ or Ba^+-Coulomb crystal stored in the trap. We present a technique to achieve a reliable positioning of the molecular ions after separating them from the crystal at repetition rates on the order of 1 kHz or higher. The reloading scheme operates on axis of the linear Paul-trap and bases on dissipative interaction between the crystal and the molecular ions. This provides us with a source for cold and located charged molecules as targets for time resolved electron diffraction. Our electron gun should emit short electron bunches using recent developments of short and intense laser facilities. It is expected that the diffracted electrons will provide us with information about synchronized and photo triggered structural changes of molecules on a short timescale. Further developments such as the alignment of the molecular ion by fs-laser pulses, internal cooling and the generation of even shorter electron pulses or implementing X-ray pulses should considerably increase the efficiency and suitability of the apparatus and can be discussed.

Supported by: IMPRS, MAP, MPG

MO 29.6 Di 16:30 Poster A

Ein langer Stark-Abbremser für Schwefeldioxid — •Oleg Bucicov, Marcin Nowak, Sebastian Jung, Eberhard Tiemann und Christian Lisdat — Leibniz Universität Hannover

Wir werden einen Stark-Abremser für niedrig-Feld-suchende Zustände mit 326 Stufen vorstellen. Mit diesem Experiment wird es möglich sein, das relativ schwere SO_2 Molekül bis zum Stillstand abzubremsen. Der Aufbau ist die Weiterentwicklung eines erfolgreich getesteten Stark-Abremsers mit 140 Stufen [1]. 326 Stufen sind notwendig, um SO_2 abzubremsen, da das Verhältnis von Stark-Energie zu kinetischer Energie trotz des groß Dipolmomentes von SO_2 sehr ungünstig ist.

Mit dem abgebremsten, kalten Schwefeldioxid werden dann Experimente zu Photodissoziation durchgeführt. Durch die Möglichkeit der Photodissoziation direkt an der Schwelle können die Fragmente SO und O zustandsselektiv ebenfalls kalt erzeugt werden. Die Überschußenergie ist durch externe Felder einstellbar [2].

[1] S. Jung *et al.*, Phys. Rev. A **7**4, 040701(R), 2006.
[2] S. Jung *et al.*, J. Phys. B **3**9, S1085, 2006.

MO 29.7 Di 16:30 Poster A

Collisions between cold, trapped ND_3 and hot gases — •Christian Sommer, Sebastian Pohle, Thomas Rieger, Laurens D. van Buuren, Pepijn W.H. Pinkse, and Gerhard Rempe — Max-Planck-Institut für Quantenoptik, Hans

Currently, there is a wide interest to trap cold molecules at temperatures around 1 Kelvin [1]. At high densities cold collisions and chemical reactions can be studied, whereas the low velocities and long storage times permit high-resolution spectroscopy. Besides, these traps could form the starting point for a second cooling mechanism, such as evaporation, to bring molecules into the ultra-cold regime.

In previous experiments our group demonstrated filtering and trapping of slow polar molecules from an effusive source using an electrostatic guide and storage trap [2]. For ND_3, trap densities up to 10^8 molecules/cm^3 were obtained with a 130 ms life time.

Here, we investigate the trap losses of ND_3 molecules due to collisions with several room-temperature gases. A constant background

pressure in the trap environment is obtained by adding a constant flow of gas with a needle valve. From the data taken at several background pressures, cross sections are inferred. These can be used to estimate collisional losses in future trap geometries or in gaseous environments.

[1] J. Doyle, B. Friedrich, R.V. Krems and F. Masnou-Seeuws, European Physical Journal D **31**, 149 (2004)
[2] T. Rieger, T. Junglen, S.A. Rangwala, P.W.H. Pinkse and G. Rempe, Physical Review Letters **95**, 173002 (2005)

MO 29.8 Di 16:30 Poster A

NaK beam experiments: Cold Collision Studies — Andreas Gerdes, Matthias Hobein, •Alexander Stein, Horst Knöckel, and Eberhard Tiemann — Institut für Quantenoptik, Gottfried Wilhelm Leibniz Universität Hannover, Welfengarten 1, 30167 Hannover

Investigation of the potential energy curves (PEC) of singlet and triplet electronic ground states of mixed alkalis allows for the description of cold collisions deriving characteristic properties of the system like scattering lengths or Feshbach resonance positions [1]. Heatpipe measurements were performed as a first approach to the energy structure of the starter molecule NaK. The detailed analysis of the spectra taken in the heatpipe setup will be presented as well as first steps with NaK at a new built beam setup (characterization of the beam conditions). Furthermore first results of experiments supplemental to the heatpipe data will be shown. Most interesting for prediction of scattering properties are the high lying rovibrational levels in the potential to study cold collision spectroscopy as already shown for Na_2 [2]. The next step to the very actual case of KRb (cold molecules produced in a trap) has come into reach.
[1] A. Crubellier *et al.*, Eur. Phys. J. D **6**, 211-220 (1999)
[2] O. Docenko *et al.*, J. Phys. B: At. Mol. Opt. Phys. **39** 929-943 (2006)

MO 29.9 Di 16:30 Poster A

Blackbody thermometry with cold molecular ions and possible application to ion-based frequency standards — •Jeroen Koelemeij, Bernhard Roth, and Stephan Schiller — Institut für Experimentalphysik, Universität Düsseldorf

We have used laser spectroscopy to measure the rotational level distribution of trapped molecular HD^+ ions at translational temperatures in the millikelvin range. Under our experimental conditions, the internal (rotational) degrees of freedom turn out to be independent of the translational degrees of freedom, and an effective rotational temperature close to room temperature is found. The near absence of background-gas collisions allows to relate the rotational temperature directly to the temperature of the ambient blackbody radiation (BBR). This feature suggests the use of molecular ions for BBR thermometry, which may help to improve the accuracy of frequency standards based on trapped atomic ions. We present a detailed proposal for the implementation of BBR thermometry, using CO^+ molecular ions, in a generic trapped-ion optical clock apparatus. Our proposal includes a method to load CO^+ by photoionization of neutral CO in the residual gas, while BBR thermometry would be based on a novel scheme for nondestructive detection of rotational states of CO^+.

MO 29.10 Di 16:30 Poster A

Experiments with decelerated and trapped OH radicals — •Joop Gilijamse[1], Steven Hoekstra[1], Nicolas Vanhaecke[2], Ludwig Scharfenberg[1], Sebastiaan van de Meerakker[1], and Gerard Meijer[1] — [1]Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany — [2]Laberatoire Aime Cotton, CNRS II, Campus d'Orsay, France

With a Stark decelerator, bunches of state-selected molecules with a controlled velocity and with longitudinal temperatures as low as a few mK can be produced. We will report on the deceleration and electrostatic trapping of ground state OH and OD radicals. The trap loading has been optimized using evolutionary strategies, and using a new trap geometry. The radicals are trapped at a density of 107 * 108 cm-3 and at a temperature in the 50-500 mK range. The blackbody radiation limited trap lifetime is measured to be 1.9 s and 3.7 for the OH and OD radical, respectively. Recent experimental results illustrate two unique features of our experimental method: the long interaction time afforded by the trap and the high energy resolution of the velocity-tunable molecular beam.

MO 29.11 Di 16:30 Poster A

Manipulating molecules in high-field seeking quantum states with electric fields — •Frank Filsinger, Kirstin Wohlfart, Jochen Küpper, and Gerard Meijer — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany

The manipulation of molecules in low-field seeking quantum states with electric fields is a well established technique today. A wide range of applications, from simple electrostatic focusing devices to sophisticated tools such as Stark decelerators, have been realized.

However, the ground state of every molecule and, for larger (bio-)molecules, practically all states that are populated in a molecular beam, are high-field seeking. Therefore, similar tools for molecules in high-field seeking quantum states are highly desirable. Recently it has been shown, that molecules in high-field seeking quantum states such as metastable CO, YbF, and benzonitrile can be focused and decelerated using switched electric fields in an Alternate Gradient decelerator [1]. These techniques can also be used to specifically manipulate individual structural isomers of large (bio-)molecules.

We discuss the behaviour of molecules in high-field seeking quantum states in the practically relevant electric fields. A profound understanding of the Stark effect of large molecules, their focusing properties, and possible loss mechanisms (e.g. Majorana transitions) is essential for these experiments.
[1] H.L. Bethlem, M.R. Tarbutt, J. Küpper, D. Carty, K. Wohlfart, E.A. Hinds, and G. Meijer, *J. Phys. B*, **39**, R263-R291, (2006)

MO 29.12 Di 16:30 Poster A

Majorana transitions and their compensation in electric Ioffe-Pritchard traps — •Moritz Kirste, Melanie Schnell, Hendrick L. Bethlem, and Gerard Meijer — Fritz-Haber-Institut der MPG, Abt. Molekülphysik, Faradayweg 4-6, D-14195 Berlin

Trapping of polar molecules with the use of the Stark effect is possible. Due to the Stark effect the molecules separate in low field seeking and high field seeking states. The low field seeking molecules can be trapped in the minimum of an electrostatic quadrupole trap. Trapped molecules are used in the study of dipole-dipole interaction and of the alignment of molecules in external fields as well as in the application of high-resolution spectroscopy. All these techniques are limited by the quality of the trap - the time the molecules remain in the trap and the trap depth - which is itself limited by the loss rate of the trap. Trap losses are caused by inelastic collisions of the electrostatically trapped molecules and by Majorana transitions. This poster gives a short overview of the theoretical background of Majorana transitions and their influence on electrostatically trapped ND3.

The Majorana losses in electrostatic quadrupole traps can be compensated by the use of a so called Ioffe-Pritchard trap. A Ioffe-Pritchard trap generates a quadrupole field which is non-zero at the center. They have already been realized for magnetic fields but not yet for electrostatic fields. This poster introduces different types of possible electric Ioffe-Pritchard trap configurations and discusses their advantages and disadvantages.

MO 30: Poster: Spectroscopy in He droplets

Zeit: Dienstag 16:30–18:30 Raum: Poster A

MO 30.1 Di 16:30 Poster A

Characterisation of the Even-Lavie nozzle as a source for a pulsed helium nanodroplet beam — •Christoph Strauss, Oliver Bünermann, Marcel Mudrich, and Frank Stienkemeier — Universität Freiburg, Physikalisches Institut, D-79104 Freiburg, Germany

We present first measurements with the Even-Lavie valve to characterise the flux and the peak intensity of a pulsed He droplet beam. Both mass-spectrometric measurements of the undoped beam as well as surface ionization detection of alkali-doped helium droplets were performed. The nozzle is designed for high repetition rates up to 1000Hz at temperatures down to 10K. Due to the short opening time (20μs) high peak intensities can be generated at moderate pumping speeds in the source chamber. Because of a low electric power consumption (< 3W) and an efficient cooling of the copper housing of the Even-Lavie valve, the low cooling power of a standard closed cycle refrigerator establishes cryogenic conditions. Eventually, the pulsed source will be used in combination with kHz laser ablation and kHz femtosecond lasers.

MO 30.2 Di 16:30 Poster A

Doping of helium nanodroplets by high repetition rate laser ablation — •Benjamin Forkl, Severin Müller, Marcel Mudrich, and Frank Stienkemeier — Physikalisches Institut, Universität Freiburg, Germany

In recent years helium nanodroplets have been established as an almost ideal matrix for spectroscopical studies of atoms and molecules. By evaporation of helium atoms they can dissipate energy introduced by the species under study, thus cooling molecules and complexes down to millikelvin temperatures, well below the energy needed to excite the samples vibrational degrees of freedom. By sequential doping with different atoms the droplets can be used as nanoreactors to synthesize novel complexes, thereby extending the possibilities for spectroscopic studies. In the most straightforward fashion the droplets are doped by pick-up of dopant particles from the gas phase. Since thermal evaporation is hard to achieve for high refractory metals, ions or fragile biological molecules, a pulsed laser ablation source has been constructed. An ablation laser is focused on the dopant material, thus generating a plasma in the droplet formation region providing gas phase densities of atoms, molecules or ions to be picked-up by the droplet beam. First measurements are presented of the new ablation source employing a kHz repetition rate laser.

MO 30.3 Di 16:30 Poster A

Modelling the shift and broadening of absorption lines of alkali metal atoms attached to helium nanodroplets — •Severin Müller[1], Oliver Bünermann[1], Frank Stienkemeier[1], and Manuel Barranco[2] — [1]Universität Freiburg, Physikalisches Institut, D-79104 Freiburg, Germany — [2]Departament E.C.M., Facultat de Física, Universitat de Barcelona, E-08028, Spain

In the context of helium nanodroplets alkali metal atoms are of special interest. Whereas most picked up atoms submerge in the liquid helium droplets, alkali metals reside in a dimple on the surface. The absorption spectra of the first electronic state of all stable alkali atoms are experimentally available. Though theory already addressed these systems, the shifts and broadenings of the spectra are still not fully understood. We applied a simple model treating the system droplet-alkali atom as a diatomic molecule to calculate the helium-induced shift and broadening of excitation lines. The helium density distribution of the alkali-helium droplet system used in these calculations are taken from data derived from density functional theory by M. Barranco et al [1]. In this way we are able to attribute the splitting of absorption lines and a shoulder of the absorption on the red side of the main line to the excitation to different vibrational modes of the alkali-helium molecular system. Furthermore, the droplet size dependence and the influence of the helium isotope on the absorption spectra of light alkali atoms can be reproduced.

[1] F. Stienkemeier, O. Bünermann, R. Mayol, F. Ancilotto, M. Barranco and M. Pi, Phys. Rev. B 70, 214509 (2004)

MO 30.4 Di 16:30 Poster A

Spectroscopy of PTCDA Complexes in Helium Nanodroplets — •Matthieu Dvorak and Oliver Bünermann — Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg

PTCDA (3,4,9,10 perylen-tetracarboxylic dianhydride) is a planar organic semi-conducting molecule. It became a model system for organic semiconductors because of the well-ordered films formed on surfaces. Attaching this molecule to helium nanodroplets is one of the best methods to collect very precise spectroscopic information. Due to the very low temperature (0.4 K) and the superfluid properties, helium nanodroplets provide a very cold and weak interacting matrix, ideal for spectroscopic measurements. The ability to form complexes of a desired composition via successive doping opens the way to probe oligomers and size effects. The previous studies obtained in our group concerning PTCDA [1] are extended into the blue und UV spectral region. Spectra of the monomer transition as well as the excitonic transition for PTCDA stacks were collected. Comparison with theory and film spectra quantify the red shift for monomer and excitonic transition of PDTCA films.

[1] M. Wever and F. Stienkemeier, PRB 67, 125201 (2003)

MO 30.5 Di 16:30 Poster A

Spektroskopie von Erdalkaliatomen in ^{3}He- und ^{4}He-Nanotröpfchen — •Adrian Zimmer, Oliver Bünermann und Frank Stienkemeier — Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str.3,79104 Freiburg

Heliumnanotröpfchen stellen eine sehr kalte, schwach wechselwirkende Matrix für spektroskopische Messungen zur Verfügung. Die meisten der zu untersuchenden Einlagerungen sind dabei im Inneren der Tröpfchen gebunden. Nur Alkali- und Erdalkaliatome bilden Ausnahmen mit äußerst geringen Wechselwirkungen und Bindungen auch an die Oberfläche von Heliumnanotröpfchen. Alle stabilen Erdalkaliatome bis auf Beryllium wurden in Heliumnanotröpfchen spektroskopisch charakterisiert. Die Eindringtiefe der Erdalkaliatome in Heliumnanotröpfchen wurde mit Hilfe von Absorptionsspektren im Vergleich mit Spektren in flüssigem Helium untersucht. Dabei sind im Falle von ^{4}He alle Erdalkaliatome bis auf Magnesium in einer tiefen Mulde an der Oberfläche gebunden. Eine interessante Frage ist, wie die Erdalkaliatome an ^{3}He-Tröpfchen gebunden sind. Wir haben dazu den $5s5p^1P_1^o \leftarrow 5s2^1S_0$ Übergang des Strontium sowie den $4s4p^1P_1^o \leftarrow 4s2^1S_0$ von Kalzium auf ^{3}He-Nanotröpfchen mittels Absorptionsspektroskopie untersucht. Vergleich der Ergebnisse mit entsprechenden Spektren an ^{4}He-Tröpfchen und Spektren in flüssigen Helium deuten auf eine Bindung der Atome im Inneren der ^{3}He-Tröpfchen hin. Der Befund wird durch aktuelle theoretische Rechnungen [1] bestätigt.

[1] A. Hernando, R. Mayol, M. Pi, M. Barranco, F. Ancilotto, O. Bünermann and F. Stienkemeier, in Vorbereitung

MO 31: Poster: Quantum Chemistry (Theory)

Zeit: Dienstag 16:30–18:30 Raum: Poster A

MO 31.1 Di 16:30 Poster A

Knotenoptimierung für Quanten-Monte-Carlo — •Raphael Berner, Annett Schwarz und Arne Lüchow — Institut für Physikalische Chemie, RWTH Aachen University, 52056 Aachen, Germany

Die Fixed-Node-Methode ist das am häufigsten verwendete Verfahren, um die Antisymmetrie einer Fermionen-Wellenfunktion in einer Diffusions-Quanten-Monte-Carlo-Rechnung (DMC) explizit zu berücksichtigen. Die dabei erhaltene Energie $E^{(FN)}$ hängt entscheidend von der Qualität der Knotenhyperfläche der verwendeten Trialfunktion ϕ ab. Ein Maß für die Güte dieser Knotenfläche ist der mittlere Abstand $\bar{\eta}$ der Knotenhyperfläche der beiden Funktionen ϕ und $\hat{H}\phi$. Löst ϕ die Schrödingergleichung exakt, so ist der lokale Wert von η überall Null. Durch eine entsprechende Parametrisierung der Wellenfunktion kann diese durch Minimierung von $\bar{\eta}$ optimiert werden. Neuere Untersuchungen ergaben, dass der lokale Wert von η von der Lage auf der Knotenhyperfläche abhängt. Von besonderem Interesse ist deshalb die Untersuchung von η an ausgezeichneten Punkten auf der Knotenfläche, wie den Koinzidenzpunkten von Elektronen gleichen Spins. Erste Ergebnisse zur Optimierung von Wellenfunktionen kleiner Atome und Moleküle mit Hilfe von $\bar{\eta}$ werden präsentiert.

MO 31.2 Di 16:30 Poster A

Relativistic 2-spinor miimanx density functional calculations for ZnO, CdO, HgO, UubO, and Cu2, Ag2, Au2, Rg2 — •Ossama Kullie and Dietmar Kolb — FB18, Uni Kassel, Heinrich-Plett Str. 40, 34132 Kassel, Germany

Fully relativistic 2-spinor Density functional calculations can be done with the help of the minimax principle. In this poster we show that the two spinor minimax method, utilizing the finite element methods (FEM), gives highly accurate values in relativistic Dirac-Fock-Slater (DFS) density functional calculations for two atomic molecules, especially considering systems with up to super heavy atoms like $UubO, Rg_2$. We demonstrated that one obtain benchmark values for bond length, vibrational frequency, and dissociation energy. We compare our result with our LCAO calculations, with literature values and with experimental values so far are available, and show that our highly accurate values shed a new light on the quality of the DFS-density functional[1].

[1] O. Kullie, H. Zhang, J. Kolb and D. Kolb, Relativistic density functional calculations using two-spinor minimax Finite-Element method and linear combination of atomic orbitals for $ZnO, CdO, HgO, UubO$, and Cu_2, Ag_2, Au_2, Rg_2

MO 41: Electronic and Radiofrequency Spectroscopy

Zeit: Mittwoch 11:30–12:30 Raum: 6B

MO 41.1 Mi 11:30 6B

Rotationsaufgelöste Fluoreszenzspektroskopie von 1s-angeregtem Stickstoff — Michael Meyer[1], •Jürgen Plenge[2], Roman Flesch[2], Andreas Wirsing[2] und Eckart Rühl[2] — [1]LIXAM, Centre Universitaire Paris-Sud, Bâtiment 350, F-91405 Orsay — [2]Physikalische und Theoretische Chemie, Institut für Chemie und Biochemie, Freie Universität Berlin, Takustr. 3, 14195 Berlin

Photoionisation und Autoionisation von Molekülen führen zu einer *Verteilung der Überschussenergie* zwischen dem Photoion und dem austretenden Elektron und damit zu einer Veränderung der Besetzung rotatorischer Niveaus. Bisher liegen kaum Untersuchungen zur rotatorischen Energieverteilung bei resonanten Auger-Prozessen vor, die bei der Rumpfniveauanregung von Molekülen auftreten. Durch UV/VIS-Spektroskopie kann im Gegensatz zur Augerelektronenspektroskopie die *rotatorische* Verteilung elektronisch angeregter Kationen, die durch den resonanten Auger-Zerfall innerschalenangeregter Molekülzustände auftreten, präzise gemessen werden. Wir präsentieren erstmals rotationsaufgelöste UV/VIS-Spektren molekularer Stickstoff-Ionen (N_2^+ B→X-übergang), die durch den resonanten Auger-Zerfall des innerschalenangeregten $1s^{-1}2p^1_{\pi^*}$ $(^1\Pi)$-Zustandes (E=400.88 eV) gebildet werden. Die rotatorische Struktur unterscheidet sich stark von derjenigen, die bei direkter Photoionisation aus der Valenzschale erhalten wird. Dies erlaubt es, Rückschlüsse auf den Mechanismus des resonanten Auger-Zerfalls zu ziehen.

MO 41.2 Mi 11:45 6B

Energieaufgelöste koinzidente Messung von Photo- und Augerelektron nach Innerschalenionisation bei CO, CF_4 und O_2 — •Volker Ulrich, Silko Barth, Sanjeev Joshi, Toralf Lischke und Uwe Hergenhahn — Max-Planck-Institut für Plasmaphysik, EURATOM Association, Boltzmannstr. 2, 85748 Garching

Mit schmalbandiger Synchrotronstrahlung wurde der normale Augerzerfall in gasförmigen Molekülen untersucht. Nach Ionisation des C1s, O1s bzw. F1s Elektrons konnte dessen Energie in selbstgebauten Flugzeitspektrometern gemessen werden. Das gleichzeitig emittierte Augerelektron wurde in einem hemisphärischen Detektor registriert und seinem entsprechenden Photoelektron zugeordnet. Als Resultat erhält man eine Koinzidenzkarte, in der die Augerenergie gegen die (ggfs. vibrationsaufgelöste) Photoelektronenenergie aufgetragen wird. Daraus lassen sich quantitativ die Franck-Condon-Faktoren vom einfach ionisierten Zwischenzustand zu den zweifach geladenen Endzuständen bestimmen sowie, falls vorhanden, die Vibrationsenergien des jeweiligen Endzustandes. Im CO stimmen die Franck-Condon-Faktoren mit den auf einfachem Niveau berechneten Werten qualitativ überein, allerdings mit Abweichungen von der Theorie in der Vibrationsenergie des B-Zustandes. Diese Messung ist eine experimentelle Bestätigung von bisher nur theoretisch beschriebenen Potenzialkurven des CO^{2+}.

Die Potentialkurve des Zwischenzustandes von CF_4^+ verläuft, im Gegensatz zu CO, dissoziativ. Mit koinzidenten Messungen kann nun festgestellt werden, ob die Präparation des Zwischenzustandes einen Einfluss auf die Population der Endzustände hat oder nicht.

MO 41.3 Mi 12:00 6B

Shaperesonanzen als stehende Photoelektronen-Wellen in kleinen Molekülen — •B. Langer[1], B. Zimmermann[2], O. Gessner[3], D. Rolles[3,4], R. Hentges[7], J. Viefhaus[5], V. McKoy[6] und U. Becker[7] — [1]Freie Universität Berlin — [2]LSU — [3]LBNL — [4]WMU — [5]DESY — [6]Caltech — [7]FHI

Shaperesonanzen bei der Photoionisation kleiner Moleküle sind ein seit vielen Jahren intensiv untersuchtes Phänomen. Insbesondere für die K-Schalenphotoionisation dieser Moleküle konnte ein interessanter linearer Zusammenhang zwischen der Bindungslänge und der Lage der Shaperesonanz oberhalb der diesbezüglichen Ionisationsgrenze gezeigt werden, der bisher weitgehend qualitativ abgeleitet und dessen Proportionalitäskonstante semiempirisch bestimmt wurde. Wir zeigen an Hand von im Molekülachsensystem richtungsaufgelösten Photoelektronenspektren, dass dieser Zusammenhang analytisch hergeleitet werden kann. Es handelt sich bei diesen Shaperesonanzen nicht um niederenergetische Ausläufer der EXAFS Oszillationen bei höheren kinetischen Energien, sondern um stehende Wellen bei $\lambda = 2R$ und $4R$, je nachdem ob die Photoelektronenwelle in das dichtere Medium bzgl. der innermolekularen Elektronendichte eintritt, oder aber aus ihm austritt. Insbesondere die prominente Shaperesonanz bei $\lambda = 4R$ führt zu einem analytischen Zusammenhang zwischen R und der kinetischen Energie des Photoelektrons auf dem Maximum der Shaperesonanz, der mit den semiempirischen Werten sehr gut übereinstimmt. Die Implikationen dieses Modells für die phasenfreie Abstandsbestimmung von Bindungslängen kleiner Moleküle werden diskutiert.

MO 41.4 Mi 12:15 6B

Die Radiospektren von 1,2,3- und 1,2,4-Tricyanobenzol — •Jens-Uwe Grabow[1], Michael Rosemeyer[1], Alberto Lessari[2], Henning Hopf[3] und Robert J. McMahon[4] — [1]Gottfried-Wilhelm-Leibniz-Universität Hannover, Institut für Physikalische Chemie, Callinstraße 3A, 30167 Hannover, Germany — [2]Universidad de Valla-

dolid, Departamento Quimica Fisica y Quimica Inorganica, Facultad de Ciencias, Prado de la Magdalena, s/n, 47005 Valladolid, Spain — [3]Technische Universität Braunschweig, Institut für Organische Chemie, Hagenring 30, 38106 Braunschweig, Germany — [4]University of Wisconsin, Department of Chemistry, 1101 University Avenue, Madison, WI 53706, USA

Aromatische Kohlenwasserstoffe und deren polyzyklische Vertreter (PAH) werden als die häufigsten interstellaren Moleküle vermutet. Unter den über 140 nachgewiesenen Spezies befindet sich jedoch neben dem IR-spektrokopisch aufgefundenen Benzol selbst kein weiterer Aromat. Möglicherweise weil PAHs nur ein kleines Dipolmoment - die Voraussetzung für einen radioastronomischen Nachweis - besitzen.

Tricyanobenzole bieten einen neuen Ansatz zum Nachweis von Aromaten: Durch Kondensation von Cyanoacetylen - im interstellaren Medium verbreitet - gebildet, besitzen sie ein beachtliches Dipolmoment.

Mit dem dem "Coaxially Oriented Beam-Resonator Arrangement Fourier-Transform Microwave (COBRA-FTMW)" Spektrometer in Hannover gelang mit der Aufkärung der zuvor unbekannten und durch dreifache Kernquadrupolkopplung komplexen Radiospektren die Voraussetzung für eine radioastronomische Suche.

MO 42: Quantum Chemistry (Theory)

Zeit: Mittwoch 11:30–12:15 Raum: 6D

MO 42.1 Mi 11:30 6D

Relativistic density functional calculations based on the 2-spinor minimax principle for diatomic molecules — •Ossama Kullie and Dietmar Kolb — FB18, Uni Kassel, Heinrich-Plett Str. 40, 341132 Kassel, Germany

The two spinor minimax method, utilizing the finite element methods (FEM), gives highly accurate values in relativistic density density functional calculations for two atomic molecules, especially considering systems with up to super heavy atoms like Rg_2. One obtain benchmark values for bond length, vibrational frequency, and dissociation energy. In our previous work we demonstrated this for Dirac-Fock-Slater (DFS) functional [1]. In present talk we show density functional calculations for different type of functionals including Non- and relativistic LDA,and eventual GGAs, functionals for the dimers of the group 11 (IB) of the periodic table Cu_2, Ag_2, Au_2, Rg_2. We compare our result with values from the literature and with the experimental values so far are available. We hope that we can, like in the case of DFS, show in a systematic way the behaviors of these functionals and shed new light on this behaviors.

[1] O. Kullie, H. Zhang, J. Kolb and D. Kolb, Relativistic density functional calculations using two-spinor minimax Finite-Element method and linear combination of atomic orbitals for $ZnO, CdO, HgO, UubO$ and Cu_2, Ag_2, Au_2, Rg_2. J. Chem. Phys. **126**, 1 (2007).

MO 42.2 Mi 11:45 6D

On the matrix singularity problem in the variational Gaussian wave packet method — •Tomaž Fabčič, Jörg Main, and Günter Wunner — 1. Institut für Theoretische Physik, Universität Stuttgart, 70550 Stuttgart

Variational solutions of the time-dependent Schrödinger equation are often based on Gaussian wave packets (GWP) as trial functions. The equations of motion for the time-dependent Gaussian parameters become ill-conditioned from time to time during the propagation, and this problem increases with the number of propagated GWP, leading to extremely small step sizes of the integration routines. On the other hand a sufficiently large number of GWP is necessary to obtain accurate results. The instabilities of the equations of motion are due to a temporary overcrowding of the set of GWP, making the set of linear equations that has to be solved after each time step of integration nearly singular. We present a novel method to overcome these numerical problems by subjecting the GWP to adequate inequality constraints, rendering the integration process orders of magnitude faster. The power of the method is demonstrated for a two dimensional non-integrable model potential.

MO 42.3 Mi 12:00 6D

Vanadium Oxide Compounds with Quantum Monte Carlo — •Annika Bande and Arne Lüchow — Institut für Physikalische Chemie, RWTH Aachen University, Landoltweg 2, 52056 Aachen, Germany

Transition metals and their compounds display an astonishing variety of all kinds of chemical systems which exhibit very different types of bonding and excitation spectra. These systems are at the forefront of electronic structure research, most appealing methods in this context are correlated ones such as configuaration interaction, coupled-cluster or quantum Monte Carlo (QMC).

In this study the QMC method has been used to calculate several vanadium oxide molecules and ions as well as the vanadium atom in the ground and different excited states. The guide functions, which consist of one or only few Slater determinants, were obtained from Hartree-Fock, density functional or multi configuration self consistent field calculations and supplemented with a Jastrow correlation factor. Different pseudopotentials were applied in order to optimize the QMC procedure in terms of efficiency to aim at extending the calculations to much larger systems and reaction pathways.

MO 51: Mitgliederversammlung des Fachverbands Molekülphysik

Zeit: Donnerstag 11:30–12:30 Raum: 6D

Dauer ca. 60 Minuten

MO 52: Femtosecond Spectroscopy IV

Zeit: Donnerstag 14:00–15:45 Raum: 6B

MO 52.1 Do 14:00 6B

Ultrafast Fluorescence Quenching in a Naphthalene Bisimide Dye — Patrizia Krok[1], •Stefan Lochbrunner[1], Alfred Błaszczyk[2], Marcel Mayor[2], and Eberhard Riedle[1] — [1]Lehrstuhl für BioMolekulare Optik, LMU München — [2]Department für Chemie, Universität Basel

Naphthalen bisimide dyes are promising candidates for molecular electronics applications since their electronic structure can be efficiently tuned by substituents. In the case of two phenyl substituted naphthalene bisimide derivatives we find that the fluorescence quantum yield [1] and the emission lifetime of the naphthalene chromophore depend strongly on the number of carbon atoms in the linker between the chromophore and the phenyl substituent. While a benzyl thio substituted derivative emits reasonably strong fluorescence from the S_1 state, the fluorescence of a phenyl thio substituted derivative is reduced by a factor of 16. In a pump-probe experiment the transient absorption of both molecules was studied after selective excitation into the S_1, S_2, or the S_3 state. The experimental traces reveal an ultrafast nonradiative decay of the higher states into S_1. The lifetime of the stimulated emission from the S_1 state is 40 ps for the fluorescent dye and only 6 ps for the nonfluorescent dye. We argue that the fast decay is the result of an electron transfer from the phenyl substituent to the chromophore. The charge transfer state has a similar lifetime of also about 6 ps, which we understand as the time for the charge recombination.

[1] A. Błaszczyk, M. Fischer, C. von Hänisch, and M. Mayor, Helvetica Chimica Acta **89** (2006), 1986.

MO 52.2 Do 14:15 6B

The Fluorescence Signature of an Ultrafast H-Transfer — •Thomas Schmierer, Björn Heinz, and Peter Gilch — Department für Physik, Ludwig-Maximilians-Universität, Oettingenstr. 67, D-80538 München, Germany

Ortho-substituted nitro-arenes find widespread application in biotechnology as photo-labile protecting groups. The primary photo-process in these compounds is believed to be an H-transfer from the *ortho*-substituent to the nitro group. For one nitro-arene, *ortho*-nitrobenzaldehyde (NBA), it has recently been demonstrated that the product of this transfer is formed in $\sim$ 400 fs [1]. Here, we report on the femtosecond fluorescence signature of this transfer which has been recorded with a Kerr gate set-up [2]. NBA absorbs in the UV and its emission is extremely weak and short-lived. Therefore, special procedures are required to realize time-resolved measurements which will be outlined in the presentation. Implications of these measurements on the mechanism of the H-transfer will be discussed.

[1] S. Laimgruber et al., Angew. Chem. Int. Ed. 44 (2005) 7901
[2] B. Schmidt et al. Appl. Phys. B 76 (2003) 809

MO 52.3 Do 14:30 6B

Mode-selective vibrational energy transfer after infrared excitation of a hydrogen-bonded OH stretching vibration — •Valeri Kozich, Wolfgang Werncke, Jens Dreyer, Satoshi Ashihara, and Thomas Elsaesser — Max-Born-Institut für Nichtlineare Optik und Kurzzeitspektroskopie, Max-Born-Strasse 2A, D-12489 Berlin, Germany

Vibrational energy relaxation in hydrogen bonds is of considerable importance for understanding ultrafast dynamics in many chemical and biological systems. We have studied the relaxation of the hydrogen-bonded OH stretching vibration of 2-(2'-hydroxy-5'-methyl-phenyl)benzotriazole (TINUVIN P) by ultrafast infrared-pump/Raman probe and infrared-pump/infrared probe spectroscopy. We determined a 200 fs lifetime for the OH stretching mode and revealed that intramolecular vibrational energy redistribution occurs through a few major channels that all involve combination and overtone bands of modes with considerable in-plane OH bending character. The most prominent role for the primary relaxation process is played by the mode with the largest OH bending contribution, thus highlighting the important role of energy transfer from stretching to bending motions in hydrogen bonds. Theoretical calculations of vibrational energy transfer rates based on a Fermi golden rule approach are in accordance with these experimental results.

MO 52.4 Do 14:45 6B

Catastrophic melting of ice at the limit of superheating — •Marcus Schmeisser, Hristo Iglev, and Alfred Laubereau — Physik-Department E11, Technische Universität München, 85748 Garching, Germany

Melting of ice is a process of universal relevance and considerable experimental and theoretical efforts have been invested to study this phenomenon. In our recent study of isotopically mixed ice [1, 2] we demonstrated that shock laser heating of bulk ice can overcome the common surface melting, leading to substantial superheating of the ice lattice.

Here, we present an experimental study of bulk melting of protonated and isotopically mixed ice. Using the recently developed ultrafast IR temperature jump technique of ice [1, 2] catastrophic melting of the excited ice lattice and further features were observed for the first time [3]. The partial melting process is accompanied by accelerated temperature and pressure decays of the residual ice component.

[1] H. Iglev, M. Schmeisser, K. Simeonidis, A. Thaller, A. Laubereau, *Nature* **439**, 183 (2006).
[2] M. Schmeisser, A. Thaller, H. Iglev, A. Laubereau, *New J. Phys.* **8**, 104+ (2006).
[3] M. Schmeisser, H. Iglev, A. Laubereau, *subm.*

MO 52.5 Do 15:00 6B

Femtosecond dynamics of the reexcited species generated from the CTTS-State in aqueous solution — •Martin K. Fischer, Hristo Iglev, and Alfred Laubereau — Physik-Department E11, Technische Universität München, 85748 Garching, Germany

The dynamics of the atom:electron-pair and the solvated electron in aqueous solution are studied using femtosecond pump-probe and pump-repump-probe techniques. After excitation of 20 mM $I^-_{(aq)}$ with a laser pulse at 200 nm wavelength in the 2nd charge-transfer-to-solvent (CTTS)-band, the resulting electron release and relaxation dynamics are investigated using probing pulses in the range 450 to 3900 nm.

Direct evidence for the second, direct detachment channel is obtained in accordance with theoretical predictions. The quantum yield of hydrated electrons is found to increase drastically as compared to excitation at 242 nm and can be traced back to a new formation channel. We will also report on novel pump-repump-probe experiments observing for the first time the atom:electron pair state predicted by quantum simulations.

MO 52.6 Do 15:15 6B

Ultrafast Excimer Formation in Perylene Bisimide Aggregates — Stefan Schindlbeck[1], •Stefan Lochbrunner[1], Volker Dehm[2], and Frank Würthner[2] — [1]Lehrstuhl für BioMolekulare Optik, LMU München — [2]Institut für Organische Chemie, Universität Würzburg

Perylene bisimide dyes are versatile building blocks in organic electronics and their aggregates represent promising functional units. 1-dimensional aggregates are generated by self-assembly of tridodecylphenyl substituted perylene bisimide molecules [1]. We investigate the electronic structure of these aggregates with femtosecond absorption spectroscopy to provide the underlying knowledge for understanding the behavior of corresponding functional units. The transient spectrum observed after optical excitation into the first electronic absorption band consists of ground state bleach and a broad and structureless excited state absorption. No indications for a reasonable strong stimulated emission are found even at short delay times down to 100 fs. This is surprising since the absorption is associated with a strong transition dipole and points to an extremely fast change in the electronic wavefunction that reduces efficiently the oscillator strength. The results are explained by the formation of excimers and a reduction of the intermolecular distance. The electronic wavefunction exhibits charge transfer character in the potential minimum whereas the S_1 character of the monomer dominates in the Franck-Condon region.

[1] F. Würthner, Z. Chen, V. Dehm, and V. Stepanenko, Chem. Commun. **2006**, 1188.

MO 52.7 Do 15:30 6B

Ultrafast Exciton Dissociation in Micro Crystalline Pentacene Films — •Henning Marciniak[1], Stefan Lochbrunner[1], Martin Huth[2], Stefan Schiefer[2], and Bert Nickel[2] — [1]Lehrstuhl für BioMolekulare Optik, LMU München — [2]Department für Physik und CeNS, LMU München

Micro crystalline thin films of organic molecules are frequently used in organic electronics applications. Their electronic structure and dynamics determine to a large extent the device behavior. We investigate with femtosecond absorption spectroscopy pentacene films prepared by vapor deposition which are used in many prototype applications. They consist of closely packed grains that are microcrystals formed by several monolayers of pentacene molecules [1]. 30 fs long pump pulses are applied to generate singlet excitons in the film. Transient spectra are measured with a white light as probe beam and time traces with compressed pulses resulting in a time resolution of 30 fs. The polarization dependent bleach spectra point to a fairly strong charge transfer character of the primary excitations. We find that the original exciton emission decays within 100 fs indicating that an ultrafast dissociation of the excitons into polarons or triplet excitons takes place. The recovery kinetics exhibits two components. One depends on the excitation energy and can be modeled with annihilation processes. A second component is interpreted as occupied traps which have a limited lifetime.

[1] B. Nickel, R. Barabash, R. Ruiz, N. Koch, A. Kahn, L. C. Feldman, R. F. Haglund, and G. Scoles, Phys. Rev. B **70** (2004), 125401.

MO 53: New Experimental Techniques

Zeit: Donnerstag 14:00–15:45 Raum: 6D

Fachvortrag MO 53.1 Do 14:00 6D

Terahertz Laserspektrometer und Bildgebung — •Erik Bründermann — Physikalische Chemie II, NC 7-68, 44780 Bochum

Wässrige Lösungen konnten bisher nur sehr schwer im THz-Bereich vermessen werden u.a. aufgrund des geringen Signal-zu-Rausch-Verhältnisses (SRV). THz-Time-Domain-Spektrometer haben typisch ein ausreichendes SRV $\geq 10^4$ für Frequenzkomponenten unterhalb von 1.5 THz, SRV ≥ 100 bei 2 THz, SRV ≥ 10 bei 2.5 THz mit jeweils 1 s Integrationszeit und Frequenzauflösungen im GHz-Bereich.

Mit einem in der Frequenz durchstimmbaren THz-Germanium-Laser hoher Leistung und gekühlten Detektoren konnten wir ein automatisiertes Table-Top Transmissionsspektrometer für in Wasser gelöste Biomoleküle realisieren [1]. Der Laser kann den Bereich von 1 bis 4 THz mit Linienbreiten im MHz-Bereich abdecken. Mit einer Integrationszeit von 0.4 ms entsprechend 100 Pulsen a 4 μs erreichen wir dann z.B. bei 2.4 THz ein SRV von mehr als 10^6 [1]. Damit ist die Messung des großen Parametersatzes aus verschiedenen Konzentrationen, Pufferlösungen, pH-Werten und Temperaturen, relevant bei biologischen Proben mit hinreichender Statistik erst möglich [1].

Weiterhin geben wir einen Ausblick auf Quantenkaskadenlaser sowie Bildgebung mit Videoraten [2] (www.rub.de/pc2/thz-video.html).

[1] U. Heugen, G. Schwaab, E. Bründermann, M. Heyden, X. Yu, D. M. Leitner, and M. Havenith, PNAS **103**, 12301 (2006).

[2] E. Bründermann et al., Opt. Express **14**, 1829 (2006); Photonik **3**, 88 (2006); Photonik **6**, 60 (2006).

MO 53.2 Do 14:30 6D

Laserspektroskopischer, kalibrationsfreier Nachweis von H_2O-Dampf mittels neuartiger $2.6\mu m$ DFB-Diodenlaser. — •Karl Wunderle, Christian Lauer, Steven Wagner, Stefan Hunsmann und Volker Ebert — Physikalisch-Chemisches Institut, INF 253, 69120 Heidelberg

Die empfindliche Feuchtebestimmung in Gasen ist sowohl in der Atmosphärenforschung als auch in vielen Industrieprozessen wie Trocknungsprozessen oder Halbleiterfertigung von zentraler Bedeutung. Die erforderliche hohe Empfindlichkeit in Kombination mit der starken Wasseradsorption stellt jedoch besondere Schwierigkeiten dar. Die Diodenlaser-gestützte in-situ Feuchtemessung bei $1.4\mu m$ ist dabei vor allem in der kalibrationsfreien Variante sehr viel versprechend, erreicht jedoch bei kurzen Wegstrecken (10cm) Nachweisgrenzen von etwa 5ppm. Neuartige $2.6\mu m$ DFB-Diodenlaser eröffnen nun erstmals den Zugang zu 20x stärkeren Absorptionslinien und somit Nachweisgrenzen bis in den ppt-Bereich, die schlechteren Detektoren und Glasfasern bei $2.6\mu m$ reduzieren jedoch den Empfindlichkeitsgewinn. Zur Minimierung dieser Einflüsse wurde eine Software zur optimierten Linienauswahl entwickelt und auf das $2.6\mu m$ System angewandt. Zur Validierung wurde, nach eingehender Charakterisierung bspw. des dynamischen Abstimmverhaltens des $2.6\mu m$ Lasers auf einem weitgehend automatisierten Messstand, ein experimenteller Vergleich des fasergekoppelten $1.4\mu m$ und des neuen $2.6\mu m$-Freistrahl-Laserhygrometers begonnen. Erste Ergebnisse dieses Vergleiches werden vorgestellt.

MO 53.3 Do 14:45 6D

Messung der Kohlendioxidkonzentration zur Überwachung bei der Sequestrierung in Aquifern — •Rozalia Orghici[1], Ulrike Willer[1,2] und Wolfgang Schade[1,2] — [1]TU Clausthal, Institut für Physik und Physikalische Technologien, Leibnizstraße 4, 38678 Clausthal-Zellerfeld — [2]TU Clausthal, LaserAnwendungsCentrum, Arnold-Sommerfeld-Straße 6, 38678 Clausthal-Zellerfeld

Eine viel versprechende Methode, Kohlendioxid aus dem atmosphärischen Kreislauf zu entfernen, ist die Verpressung in tief gelegenen Aquifern. Entsprechende Experimente zur Verpressung werden im Rahmen des EU Projektes CO_2SINK in Ketzin durchgeführt. Parallel werden innerhalb des BMBF-Projektes Chemkin Sensorkonzepte erarbeitet, die ortsaufgelöste Messungen der CO_2-Konzentration innerhalb von Bohrlöchern in Tiefen bis zu 800m erlauben. Ein Konzept ist die Anwendung der Evaneszenzfeldspektroskopie bei einer Wellenlänge von $\lambda = 1570$ nm. Ein Wellenleiterelement wird in die zu untersuchende Flüssigkeit eingeführt und die Intensitätsabnahme aufgrund der Störung der Totalreflexion in Abhängigkeit von der gelösten Gasmenge bestimmt. Es werden Labormessungen zur Messung unterschiedlicher CO_2-Konzentrationen vorgestellt, die bei bis zu 90 bar Umgebungsdruck durchgeführt wurden und mit Messungen in der Gasphase verglichen.

MO 53.4 Do 15:00 6D

Broadband Multiplex CARS Microscopy employed for Polymer Analytics — •Bernhard von Vacano, Lars Meyer, and Marcus Motzkus — Physikalische Chemie, Philipps-Universität Marburg, D-35032 Marburg, Germany

Broadband multiplex coherent anti-Stokes Raman Scattering (MCARS) microscopy can be implemented with a single laser using supercontinuum generation in a photonic crystal fiber.[1,2] In such a scheme, a spectrally narrow portion of a femtosecond oscillator is employed as pump and probe frequency components, while the remaining pulse energy is used to create a broadband Stokes supercontinuum, covering at once a vibrational range of more than 2000 cm^{-1}. This robust approach allows rapid chemical mapping of material samples with three-dimensional spatial resolution. A successful MCARS implementation and applications are presented for the identification and mapping of polymer blends. An evolutionary fitting routine is used for a fully quantitative analysis of the spectral signatures resulting in high contrast chemical maps.

[1] T. W. Kee and M. T. Cicerone, Optics Letters 29, 2701 (2004).
[2] H. Kano and H. Hamaguchi, Applied Physics Letters, 86 (2005).

MO 53.5 Do 15:15 6D

Surface Enhanced Raman Scattering (SERS) on Lithographically Fabricated Nano-Structured Gold Surfaces — •Malte Sackmann, Torsten Balster, and Arnulf Materny — International University Bremen (Jacobs University Bremen as of spring 2007), Germany

Raman spectroscopy is a valuable tool for the characterization of molecular properties and for chemical analysis. However, for low concentrations standard Raman techniques cannot be used. Making use of the enhancement of the Raman scattered signal by rough silver or gold surfaces or nano clusters the vibrational spectra even of extremely small amounts of substances could be detected. Due to the unpredictable characteristics of these substrates SERS (Surface Enhanced Raman Scattering) was nearly exclusively used for qualitative investigations. Recently, we have published first results on SERS using lithographically fabricated nano-structured gold surfaces (2dim dot gratings). However, the experimentally found enhancement factors were smaller than the expected ones by a factor of 1000. Therefore, we have now concentrated on a systematic investigation of the Raman enhancement. For this, parameters like dot sizes, shapes, and spacings were varied to find the maximum enhancement factors and also to gain better insight into the mechanisms contributing to the SERS effect. In our contribution we discuss the results of these experiments. Special emphasis is put on the question, how reproducible SERS spectra can be obtained using such well-defined substrates. This would be of great importance for possible applications in quantitative chemical analysis.

MO 53.6 Do 15:30 6D

Generation of Vector Modes with a twisted nematic Spatial Light Modulator — •Alexander Jesacher, Christian Maurer, Severin Fürhapter, Stefan Bernet, and Monika Ritsch-Marte — Division for Biomedical Physics, Innsbruck Medical University, Innsbruck, Austria

During the last decade, liquid crystal technology has found several applications in applied optics. Highly miniaturized displays with pixel sizes in the range of micrometers can be used to produce nearly arbitrary phase diffractive structures. Consequently, these devices which are also called “spatial light modulators” or “SLMs” are ideal tools for mode shaping tasks.

In some areas of research, it is desirable not only to control the phase of a light field but also its polarization state. Especially in the regime of highly focussed laser beams, where the scalar wave equation is not applicable, differences in polarization lead to significantly different intensity distributions. We demonstrate how the generation of radially and azimuthally polarized Laguerre-Gaussian and Hermite-Gaussian laser modes can be performed by using a twisted nematic liquid crystal display.

MO 54: Poster: Electronic Spectroscopy

Zeit: Donnerstag 16:30–18:30 Raum: Poster A

MO 54.1 Do 16:30 Poster A

Photophysikalische Eigenschaften von Cyanin-Farbstoffen gebunden an Nukleinsäure — •Nils Krebs — Institut für Physik, Humboldt-Universität zu Berlin , Germany

Die Lumineszenzeigenschaften der Cyanin-Farbstoffe Thiazole Orange (TO) und NIR-667 in freier und kovalent gebundener Form an Peptidnukleinsäure (PNA) wurden mittels stationärer und zeitaufgelöster optischer Spektroskopie untersucht. Die Farbstoffe zeigen eine hohe Sensitivität der Lumineszenz: bei stark viskoser Umgebung steigt die Fluoreszenzquantenausbeute und das Fluoreszenzabklingen wird länger. Bei der gebundenen Form ist TO als synthetische 'Base' kovalent in die PNA eingebunden, NIR-667 über einen Linker an das Ende des PNA-Rückgrats. Untersuchungen wurden an mit einem und mit beiden Farbstoffen markierter PNA mit verschiedenen Basensequenzen, als Einzelstrang und nach Hybridisierung mit DNA, mit und ohne Basenfehlpaarung im Duplex, durchgeführt. Mit je nur einem Farbstoff markierte PNA zeigte nach Hybridisierung mit DNA eine Zunahme der Absorption und Fluoreszenzintensität. Letztere zeigte bei fast allen untersuchten Basensequenzen eine geringere Intensität bei Vorhandensein einer Basenfehlpaarung im Duplex. Zeigaufgelöste Messungen der TO markierten PNA ergaben ein bis zu vierfach exponentielles Fluoreszenzabklingen. Dieses wurde aufgrund der Umgebungssensitivität von TO auf die Existenz von unterschiedlichen Konformationen der PNA-DNA-Moleküle zurückgeführt. Bei der zweifach markierten PNA erfolgte der Fluoreszenz Resonanz Energie Transfer (FRET) von TO zu NIR-667.

MO 54.2 Do 16:30 Poster A

Partially automated analysis of LiCs laser induced fluorescence spectra — •Alexander Stein[1], Asen Pashov[2], Peter Staanum[1], Horst Knöckel[1], and Eberhard Tiemann[1] — [1]Institut für Quantenoptik, Gottfried Wilhelm Leibniz Universität Hannover, Welfengarten 1, 30167 Hannover — [2]Department of Physics, Sofia University, 5 James Bourchier Boulevard, 1164 Sofia, Bulgaria

The precise knowledge of excited states of alkali dimers is for example of importance for the formation of cold molecules by photoassociation[1] and subsequent stimulation to ro-vibrational levels of the ground state. A powerful method for gaining this information is the evaluation of laser induced fluorescence spectra dispersed by a high resolution Fourier-transform spectrometer and additionally producing rotational satellite lines by higher buffer gas pressures[2]. Because the assignment of this huge number of transitions is very time consuming and error-prone a special software for a partial automatization of this analysis was developed. The program has been successfully applied to the spectra of LiCs measured originally for the precise determination of the ground state[3]. The program and the resulting potentials for the $B^1\Pi$ and $D^1\Pi$ state of LiCs will be presented.

[1] S. D. Kraft *et al.* J. Phys. B **39** 993, 2006.
[2] O. Docenko *et al.* Eur. Phys. J. D **36** 49, 2005.
[3] P. Staanum *et al.* submitted to Phys. Ref. A, 2006.

MO 55: Poster: Photochemistry

Zeit: Donnerstag 16:30–18:30 Raum: Poster A

MO 55.1 Do 16:30 Poster A

Suche nach ESPT-Farbstoffen — •Gregor Jung und Alexander Schmitt — Biophysikalische Chemie, Universität des Saarlandes

Die Erhöhung der Säurestärke aromatischer Alkohole und Ammoniumionen durch elektronische Anregung wurde zunächst an Pyrenderivaten und später auch an Naphtholderivaten gefunden. Die photochemische Freisetzung von Protonen im angeregten Zustand (excited state proton transfer, ESPT) wird in diesen Systemen durch die Absorption von nahem UV-Licht erreicht; der resultierende, deprotonierte Zustand fluoresziert bathochrom verschoben. Der hohe Energieinhalt der Strahlung geht allerdings mit einer geringen Photostabilität einher. ESPT-Farbstoffe im sichtbaren Bereich des elektromagnetischen Spektrums sollten daher eine höhere Photostabilität aufweisen und dann bei guter Fluoreszenzquantenausbeute auch prinzipiell für die Spektroskopie an individuellen Molekülen geeignet sein. In unserem Beitrag diskutieren wir verschiedene physikochemische Parameter, die die Bereitschaft angeregter organischer Farbstoffe zum ESPT charakterisieren. Thermodynamische Aspekte können aus den Fluoreszenzanregungs- und *emissionsmaxima abgeleitet werden, während die Lösungsmittelabhängigkeit dieser Spektren einen Einblick in die Kinetik des ESPT erlaubt. Neben den bekannten ESPT-Farbstoffen Pyrenol und Pyranin stellen wir auch einen neuen ESPT-tauglichen Farbstoff mit roter Fluoreszenz vor.

MO 55.2 Do 16:30 Poster A

Ultraschnelle photochrome Schalter: Indolylfulgide und Indolylfulgimide — •Thomas Brust[1], Stephan Malkmus[1], Simone Draxler[1], Florian Lederer[1], Christine Schulz[2], Steffen Dietrich[2], Karola Rück-Braun[2], Wolfgang Zinth[1] und Markus Braun[1] — [1]Ludwig-Maximilians-Universität München, Lehrstuhl für BioMolekulare Optik, Oettingenstraße 67, 80538 München — [2]Technische Universität Berlin, Institut für Chemie, Straße des 17. Juni 124, 10623 Berlin

Photochrome molekulare Schalter, deren reversible strukturelle Änderungen durch optische Anregung induziert werden, sind interessante Kandidaten für Anwendungen, wie zum Beispiel optische Speicher. Die Klasse der Indolylfulgide und Indolylfulgimide zeichnet sich hierbei durch die thermodynamische Stabilität ihrer Isomere aus.

Wir untersuchen die Schaltvorgänge dieser Moleküle mittels Femtosekunden-Laserspektroskopie im sichtbaren und ultravioletten Spektralbereich in einem Anrege-Abtast-Experiment. Hier soll die Dynamik der Ringöffnungsreaktion [1] vorgestellt werden. Es werden Zeitkonstanten von unter 10 ps beobachtet.

Außerdem kann die Quantenausbeute der Ringöffnung durch Zuführung thermischer Energie und optischer Überschussenergie unterschiedlich beeinflusst werden. Mit den gewonnenen Ergebnissen kann man die Reaktionsraten bestimmen und ein Barrieremodell im angeregten Zustand ableiten.

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

MO 56: Poster: Femtosecond Spectroscopy

Zeit: Donnerstag 16:30–18:30 Raum: Poster A

MO 56.1 Do 16:30 Poster A

High Harmonic Imaging of Conical Intersections — •Markus Gühr[1,2], Brian McFarland[1,2], Joseph Farrell[1,2], and Philip Bucksbaum[1,2] — [1]Stanford PULSE Center, SLAC, Menlo Park CA 94025, USA — [2]Physics Department, Stanford University, Stanford CA 94305,USA

Conical intersections (CI) are crucially involved in light harvesting, primary visual processes, DNA UV stabilization and atmospheric chemistry. A wave packet typically moves through the intersection on a femtosecond time scale, demonstrating the need for ultrafast tools that are sensitive to the electronic state change occurring in passing the CI. We theoretically propose a novel femtosecond pump-probe scheme for CIs based on high harmonic generation (HHG). A first pulse (pump)

creates a molecular wave packet on excited electronic surfaces, and the time delayed, high intensity probe pulse produces HHG on the excited molecule as it moves through the CI region. We use the symmetry of the electronic wave functions [1] to detect the electronic state change in the CI via HHG. Furthermore, we can use two center interference effects in the HHG [2,3] to determine the nuclear dynamics that is accompanied by the CI passage. To demonstrate our scheme, we perform simple model calculations on the triatomic molecule SO_2, which will be ideally suited for future experiments because of its high UV excitation cross sections for pumping the wave packet to the CI region.

[1] J. Itatani et al, Phys. Rev. Lett., 94, 123902 (2005)
[2] M. Lein et al, Phys. Rev. A, 66, 023805 (2002)
[3] T. Kanai et al, Nature, 435, 470 (2005)

MO 56.2 Do 16:30 Poster A

Schwingungsrelaxation und Prädissoziation, Dephasierung und Dispersion : Br_2 in festem Argon — •Mónika Héjjas[1], Heide Ibrahim[1], Markus Gühr[2] und Nikolaus Schwentner[1] — [1]FU Berlin, Institut für Experimentalphysik, Arnimallee 14, 14195 Berlin — [2]Stanford PULSE Center, Varian Physics Bldg., 382 Via Pueblo Mall, Stanford CA 94305-4060, USA

Wir untersuchen an einem modellartigen System die Dynamik von molekularen Wellenpaketen für den Fall, dass die Schwingungsfreiheitsgrade des Moleküls an eine Vielzahl von Schwingungsmoden eines umgebenden Bades ankoppeln können. Damit enthält diese Dynamik mehrere Effekte, die eine Amplituden- und Phasenmodulation der Pakete bewirken:(1.) Die reversible Dispersion, die von der Anharmonizität der elektronischen Potentiale des Moleküls herrührt und zu Revival-Effekten führt; (2.) Den irreversiblen Verlust von Phaseninformation an das Bad durch Schwingungsdephasierung; (3.) Energiedissipation in Form von Schwingungsrelaxation; (4.) Amplitudenverlust infolge umgebungsinduzierter Prädissoziation. Auf der Zeitskala von mehreren Femto- bis einigen Pikosekunden zeigt die Dynamik der Wellenpakete die Auswirkungen dieser Prozesse in korrelierter Form. Wir beobachten die Schwingungswellenpaketdynamik mittels Femtosekunden-Pump-Probe-Spektroskopie an Brom in einer Argon-Matrix. Wir zeigen wie sich mithilfe von Simulationen und durch Variation der Pump- und Probe-Wellenlänge, Polarisation und Dauer der Pulse, diese verschiedenen Prozesse entkoppeln lassen, sodass eine Ableitung der charakteristischen Zeiten möglich wird.

MO 56.3 Do 16:30 Poster A

Collision-induced decay of rotational coherence of N_2-molecules — •Philipp Giese, Nina Owschimikow, and Nikolaus Schwentner — FU Berlin, Institut für Experimentalphysik, Arnimallee 14, 14195 Berlin

Interaction of the anisotropy polarizability $\Delta\alpha$ of a molecule with a short and intense linearly polarized laser pulse induces a transient recurrent alignment of the molecular axis along the field dirction. The revivals of the rotational wave packet are probed via the optically induced Kerr effect. In gases at atmospheric pressure, the rotational coherence persists for several hundred ps. Populations and phases are modified only by bimolecular collisions, which makes gases an ideal model system to study the dynamics of alignment. We nonadiabatically create a rotational wavepacket using IR laser pulses (785 nm) of 150 fs duration with a power density of 10^{12} W/cm^2, and subsequently monitor the collision-induced decay of the rotational revivals in pure N_2 as well as mixtures of N_2/O_2 and N_2/Ar at pressures up to 3 atm. The experimental results are compared with models [1] and [2] for the influence of the environment. The investigations are extended to higher densities up to molecular dopants in crystalline matrices.
[1] S.Ramakrishna, T. Seideman *J. Chem. Phys.* **124**, 244503 (2006)
[2] B. Lavorel et al. *J. Raman Spectr.* **31**, 77 (2000)

MO 56.4 Do 16:30 Poster A

Calculation and shaping of CARS spectra including rotations — •Jörg Liebers[1,2], Soroosh Pezeshki[1], Michael Schreiber[2], and Ulrich Kleinekathöfer[1] — [1]International University Bremen (Jacobs University Bremen as of spring 2007), Campus Ring 1, 28759 Bremen — [2]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]. Here we use the theoretical tool of optimal control [2] to influence resonant and non-resonant femtosecond time-resolved coherent anti-Stokes Raman scattering (CARS) signals and spectra. The calculations are done by using time-dependent rotational and vibrational wave packet calculations together with perturbation theory in the laser field strength. For the non-resonant transitions an effective Schrödinger equation [3] is used to include the off-resonant states. The CARS signals can then be determined using the wave packets of different order in the field strength.
[1] J. Konradi, A. K. Singh, and A. Materny, PCCP. **7** 3574 (2005)
[2] A. Kaiser and V. May, Chem. Phys. Lett. **405** 339 (2005)
[3] D. Ambrosek, M. Oppel, L. Gonzalez, and V. May, Opt. Commun. **264** 2 (2006)

MO 56.5 Do 16:30 Poster A

Molecular Dynamics of Pigment Molecules in Mesoporous Materials: Femtosecond Studies — •Khadga Karki, Juncheng Hu, Ryan Richards, and Arnulf Materny — International University Bremen (Jacobs University Bremen as of spring 2007), Germany

Silica-based mesoporous materials like SBA, FSM, MCM, *etc.* are interesting hosts for larger pigment molecules. These materials have pore sizes ranging from 2 nm to 50 nm. The organized nano-channels, nanocages and the unique solvent nature of these materials have profound influence on the photochemistry and photophysics of the guest pigment molecules. The molecules, like chlorophyll, show remarkable photostability in these cages. Moreover, the chemical environment of the molecules can also be tuned by changing the groups on the inner surface of the cages. These interesting properties of the mesoporous materials have led to the research in organization of molecular assemblies in the cages aiming for artificial photosynthesis. In this respect, it is of interest to study how the molecular dynamics and charge transfer processes occur in the molecules caged in the functionalized nano-channels. Femtosecond studies have been performed to gain a better understanding of the molecular dynamics of the natural pigment molecules and their assemblies in the channels and cages of the mesoporous materials. In our contribution we discuss our newest results.

MO 56.6 Do 16:30 Poster A

Investigation of Molecular Dynamics in all-*trans*-β-Carotene Using Femtosecond *Pump*-FWM Spectroscopy — •Abraham Scaria, Vinu Namboodiri, Jakow Konradi, and Arnulf Materny — International University Bremen (Jacobs University Bremen as of spring 2007), Germany

The many degrees of freedom offered by four wave mixing (FWM) spectroscopy makes it a versatile tool for the investigation of complex molecular dynamics. Here, we have used *pump*-FWM spectroscopy on a femtosecond time scale to follow the molecular dynamics occurring in all-*trans*-β-carotene. The transients show clear signatures of the different spectroscopic pathways that the molecules follow after the excitation. This provides a deeper understanding of the excited state dynamics of carotenoids, which is important due to their active participation in light harvesting process. The initial pump pulse excites the molecules into the first optically accessible state (S_2). From there it undergoes a fast internal conversion (IC) in to the electronic dark state (S_1). The FWM process is chosen to be resonant with S_1 and a higher lying excited state (S_n). The results of the dependence of the initial pump power as well as the pump wavelength on the transients will be presented. Possible contributions of other electronic states are discussed.

MO 56.7 Do 16:30 Poster A

Optimal Control of CARS Spectra with Tailored Femtosecond Laser Pulses: Theory and Experiment — •Jakow Konradi, Soroosh Pezeshki, Jörg Liebers, Abraham Scaria, Vinu Namboodiri, Ulrich Kleinekathöfer, and Arnulf Materny — International University Bremen (Jacobs University Bremen as of spring 2007), Germany

The goal of coherent control in femtosecond spectroscopy is the preparation of desired quantum states of a molecule. Here, the most versatile approach is the use of suitably shaped excitation fields. In order to provide the correct pulse shapes, an exact knowledge of the molecular Hamiltonian is required, which in most cases is not available. An experimental way to solve this problem is the use of feedback-controlled learning-loop techniques. Recently, we have demonstrated the application of such an optimal control scheme for the selective excitation of vibrational modes in femtosecond time-resolved coherent anti-Stokes Raman scattering (CARS). Here, the femtosecond laser pulses were shaped in a 4f-arrangement by means of phase and amplitude modulation guided by an evolutionary algorithm. The ratio of the mode intensities in the nonlinear spectrum served as feedback for the optimization. In our contribution we are presenting the optimal control

of the femtosecond CARS spectrum of iodine. The experimental results are compared with theoretical calculations. For a simulation of the anti-Stokes spectra, the experimentally found pulse shapes were employed.

MO 56.8 Do 16:30 Poster A

Pump – Degenerate Four Wave Mixing (Pump – DFWM) as a technique for time resolving and controlling molecular excited state dynamics — •Jürgen Hauer, Tiago Buckup, and Marcus Motzkus — Physikalische Chemie, Philipps-Universität Marburg, D-35032 Marburg, Germany

Time resolving structural dynamics on short lived molecular excited states presents a challenging yet wide ranging field of ultrafast spectroscopy. We present a technique which delivers highly resolved vibrational modes as well as information on the concerned electronic states. The potential for coherent control of the observed dynamics is outlined and demonstrated on first results.

The presented method is based upon Degenerate Four Wave Mixing (DFWM). By adding an additional pump pulse preceding the DFWM – sequence (Pump – DFWM), resolving excited state dynamics becomes feasible. By chopping the pump – pulse, the observed vibrational modes can be unambiguously discerned from ground state dynamics. The time resolution achieved is only limited by the duration of the employed ultrashort laser pulses (sub 20 fs in the presented set up). Since Pump - DFWM is a pure time domain method, the spectral resolution is typically only limited by the vibrational life time. Under experimental conditions, resolution better than 20 cm^{-1} can be achieved.

Coherent control of excited state behaviour is achieved by phase modulating the pump pulse, whereas the DFWM – sequence serves as a heterodyne detection method. The effects of intuitive pulse shapes on the early excited dynamics of β carotene are discussed.

MO 56.9 Do 16:30 Poster A

Molecular Dynamics Investigation with Time-Resolved Optical Kerr Effect on CS2 - C6H6 and CS2 - PS Mixtures — •Ismael A. Heisler[1], Tiago Buckup[2], Silvio L.S. Cunha[1], and Ricardo R.B. Correia[1] — [1]Instituto de Física, UFRGS, 91501-970 Porto Alegre, Brazil — [2]Physikalische Chemie, Philipps Universität Marburg, D-35032 Marburg, Germany

The low frequency domain of the spectral density associated to the liquid state is a peculiar region where the discrimination among different relaxation processes is not so far clearly defined. To obtain information about this region, we applied time resolved heterodyne detected optical Kerr effect technique (HD-OKE) to a series of carbon disulfide - benzene (CS2-C6H6) and carbon disulfide - polystyrene (CS2-PS) mixtures. CS2-C6H6 mixtures simulate the interactions between the CS2 molecules with phenyl rings, which are the principal interacting structures present in the PS molecules. The results show that the diffusive times for pure liquids and the mixtures follow the Debye-Stokes-Einstein equation. The fast time constants were analyzed in terms of the non-diffusive component of the spectral response, which is directly associated with the molecular dynamics. The variations of the spectra were quantified and explained in terms of structural interaction configurations which produced changes in the intermolecular potential.

MO 56.10 Do 16:30 Poster A

Optimierung der Singulett-Sauerstoff-Erzeugung für die photodynamische Therapie — •Johannes Schneider, Jutta Mildner, Matthias Wollenhaupt und Thomas Baumert — Universität Kassel, Institut für Physik, Heinrich-Plett-Str.40, D-34132 Kassel

Eine effiziente Methode zum Ausschalten von kranken Zellen in der Medizin, die sogenannte photodynamische Therapie, beruht auf der lokalen Erzeugung von Singulett-Sauerstoff ($^1O_2(^1\Delta_g)$). Dabei wird ein zuvor applizierter Photosensibilisator durch Laserlicht elektronisch angeregt, gefolgt von einem Energietransfer vom Photosensibilisator zu molekularem Sauerstoff der Umgebung. Ziel der Untersuchungen ist es, die Effizienz der $^1O_2$-Produktion zu steigern und somit den Einsatzbereich der Methode in der Medizin zu erweitern.

Dazu werden neben prominenten Vertretern neu entwickelte Photosensibilisatoren (z.B. Quinoxalinoporphyrazine) in einem optisch stabilen freifließenden Flüssigkeitsfilm (Jet) präpariert und mit fs-Laserpulsen (High-Energy Oscillator, 50 fs @ 400/800 nm) angeregt. Erfolgter Energietransfer wird über die charakteristische Phosphoreszenz von $^1O_2$ bei 1270 nm per Lock-In-Detektion im fW-Bereich direkt nachgewiesen.

Ansatzpunkte für die Effizienzsteigerung der photodynamischen Therapie sind die langwellige (TiSa) Anregung der Photosensibilisatoren bei maximaler Gewebetransmission, sowie die kohärente Kontrolle des im Farbstoff stattfindenden Interkombinations-Prozesses (ISC) per Polarisations-Pulsformung im Starkfeldregime. Erste Ergebnisse der Untersuchungen werden vorgestellt.

MO 56.11 Do 16:30 Poster A

Ultrafast IR-Spectroscopy on Flavin Systems — •Matthias Wolf[1], Ruth Gross[1], Christian Schumann[1], Rolf Diller[1], Britta Person[2], and Joachim Heberle[2] — [1]Fachbereich Physik, TU Kaiserslautern, D-67663 Kaiserslautern — [2]Fakultät für Chemie, Universität Bielefeld, D-33615 Bielefeld

The function of biological blue light receptors is based on the photochemistry of the diverse flavin chromophores in the respective protein environment.

Riboflavin and flavin-adenine-dinucleotide (FAD) in solution (DMSO) were studied by sub-picosecond time resolved infrared spectroscopy. The decay of the excited electronic state on the nanosecond timescale is preceeded by vibrational cooling within a few picoseconds. These dynamics allow the identification of S_1 vibrational states as well as their spectral position.

In addition we present and discuss first measurements on the flavin mononucleotide binding LOV1 domain of the Phot1 protein from the green algae *Chlamydomonas reinhardtii*.

MO 56.12 Do 16:30 Poster A

Schwingungsspektroskopie im Femtosekundenbereich kleiner Moleküle — •Gerome Weiland, Dagmar Jones, Martin Linke, Henk Fidder und Karsten Heyne — Freie Universität Berlin, Fachbereich Physik, Arnimallee 14, 14195 Berlin

Nichtlineare schwingungsspektroskopische Untersuchungen nach elektronischer Anregung oder Schwingungsanregung wurden mit einem dreistufigen OPA an Corroles und Chloroform durchgeführt. Mehrere μJ im infraroten und nahen infraroten Spektralbereich ermöglichten die Untersuchung höherer Schwingungszustände und Mehrphotonenabsorptionsprozesse. Erste Ergebnisse dieser Untersuchungen werden präsentiert.

MO 56.13 Do 16:30 Poster A

Effects of different bridge/anchor groups on the mechanisms of ultrafast heterogeneous electron transfer in a dye/semiconductor system — •Antje Neubauer, Jodi Szarko, Carlo Dinkel, Guido Morbach, Liana Socaciu-Siebert, Rainer Eichberger, and Frank Willig — Hahn-Meitner-Institut, Glienicker Str. 100, D - 14109 Berlin

Two mechanisms for ultrafast heterogeneous electron transfer are known. For molecules bound to a TiO2 surface via a carboxylic anchor group the standard mechanism for photoinduced electron injection is widely accepted, where the chromophore of the organic dye is excited by light in a first step and the electron is injected from the excited state of the molecule in a second step. For dihydroxy compounds, where the two hydroxy groups bind to one Ti atom an alternative mechanism is known, the direct optical charge transfer.

We investigated new perylene derivatives at nano-porous colloidal TiO2 films in order to clarify the mechanisms for those heterogeneous electron transfer reactions. In these systems the perylene molecule functions as electron donor, and the wide-band gap semiconductor TiO2 functions as electron acceptor. The perylene chromophores are bound via a hydroxyl group, catechol and two hydroxy groups as bridge/anchor groups. The spectral features of the linear absorption spectra in solution and attached to TiO2 give information concerning the dynamics and therefore the mechanisms for the electron transfer, which are supported by the short time constants for the electron injection of less than 30 fs measured with transient absorption spectroscopy.

MO 56.14 Do 16:30 Poster A

Analysis and Control of Metal Cluster Reactions by Modulated Ultra-broadband Laser Pulses — •Bruno Schmidt, Shaohui Li, Xin Zhang, Aldo Mirabal, Waldemar Unrau, Juri Demuth, Torsten Siebert, and Ludger Wöste — Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin

The aim of the presented work lies in further developing femtosecond time-resolved NeNePo (negative, neutral, positive) spectroscopy within the study of catalytic reaction properties of noble metal cluster-adsorbate complexes. We seek to expand from the original analysis of the cluster dynamics to an active steering of a reactive system along

a desired coordinate through coherent control strategies. To realize this goal, ultra-broadband laser pulses are generated by means of self phase modulation through filamentation in noble gas atmosphere. Subsequently, the obtained pulses can be modulated by a liquid crystal mask within a pulse shaper setup especially designed for manipulating broadband spectra. Within these efforts, emphasis is made on characterizing the spectral phase and amplitude of the broadband, tailored pulses. This instrumentation allows for optimizing a desired reaction pathway in an active feedback loop employing genetic algorithms that control the structure of the excitation pulse. First results on the spectral properties of the continuum generation and capability of four-wave-mixing for analyzing the pulse structure will be presented.

MO 56.15 Do 16:30 Poster A

Kohärenz und Doppelspaltinterferenz bei der Doppelionisation von H2 — •Dominique Akoury[1], Katharina Kreidi[1], Thorsten Weber[2], Till Jahnke[1], Markus Schöffler[1], Lothar Schmidt[1], Ottmar Jagutzki[1], Lutz Foucar[1], Tilo Havermeier[1], Nadine Neumann[1], Horst Schmidt-Böcking[1], Reinhard Dörner[1], Tim Osipov[2], Ali Belkacem[2], Mike Prior[2], Allen Landers[3], Predrag Ranitovic[4] und Lewis Cocke[4] — [1]Institut für Kernphysik Frankfurt, Universität Frankfurt, Deutschland — [2]LBNL, 1 Cyclotron Road, Berkeley, CA 94720, USA — [3]Department of Physics, Auburn University, Auburn, Alabama 36849, USA — [4]Dept, of Physics, Kansas State University, Manhattan, KS 66506, USA

Die Emission von Photoelektronen aus einem diatomaren homonuklearen Molekül bildet ein dem klassischen Doppelspalt ähnliches System. In einer Reihe von Doppelionisationsexperimenten an H2 haben wir Interferenzstrukturen in der Elektronenwinkelverteilung relativ zur Molekülachse gefunden, die denen des klassischen Doppelspaltes ähneln. In diesen Experimenten wurden mit Hilfe der COLTRIMS Technik die Impulse beider Elektronen und Protonen in Koinzidenz gemessen. Diese Art der Messung erlaubt es, die komplexe Wechselwirkung zwischen Elektronenkorrelation und Interferenz zu untersuchen und zu verstehen.

MO 57: Poster: Quantum Control

Zeit: Donnerstag 16:30–18:30 Raum: Poster A

MO 57.1 Do 16:30 Poster A

Quantum dynamical simulations and control of light-induced molecular torsion — •Steffen Belz[1], Omar Deeb[2], Shireen Alfalah[2], and Monika Leibscher[1] — [1]Institut für Chemie und Biochemie, Freie Universität Berlin, Germany — [2]Department of Chemistry and Chemical Technology, Al-Quds University, Jerusalem, Palestinian Authority

Photochemical isomerization reactions or molecular torsion as occurring e.g. in the process of vision are currently attaining increasing interest. These light induced isomerizations which usually proceed within very short time-scales of several hundred femtoseconds [1] are governed by conical intersections between different electronic states.

In this study, we investigate molecular torsion for model systems like fulvene by means of quantum dynamical simulations. Moreover, we present the transformation of the adiabatic potential energy surfaces obtained by quantum chemical ab initio calculations into a so called diabatic representation [2,3] and point out how the pathway of the photochemical reaction depends on the structure of the conical intersection. Another aim of our study is the control of the outcome of isomerization reactions by specially designed femtosecond laser pulses. Here we show how series of two UV-laser pulses can be applied in order to increase the efficiency of the cis-trans isomerization.

[1] J.E. Kim, D. W. McCamant, L. Zhu, R.A. Mathies, *J. Phys. Chem.* B **105**, 1240 [2001].

[2] A. Thiel, H. Köppel, *J. of Chem. Phys.* **110**, 9371 [1999].

[3] M. Baer, R. Englmann, *Mol. Phys.* **75**, 293 [1992].

MO 57.2 Do 16:30 Poster A

Quantum control in strong laser fields with SPODS — Tim Bayer, •Andrea Klumpp, Dirk Liese, Cristian Sarpe-Tudoran, Andreas Präkelt, Matthias Wollenhaupt, and Thomas Baumert — Experimentalphysik III, CINSaT, Institut für Physik, Universität Kassel, Heinrich-Plett-Str. 40, D-34132 Kassel

An exciting new strong field control scenario which makes explicit use of the manipulation of the temporal phase of a pulse sequence with attosecond precision was demonstrated recently [1]. The physical mechanism of this strong field scheme is based on Selective Population of Dressed States (SPODS). Since switching between selective population of either dressed states occurs within a few femtoseconds, this technique is also interesting for applications in the presence of decoherence processes. Because SPODS combines high selectivity and tunability with efficient population transfer, relevant applications to chemistry - so far investigated theoretically [2] are within reach. In our future work we will perform experiments with shaped femtosecond laser pulses on different molecules to understand and manipulate the underlying processes of ionization and fragmentation in strong laser fields. The complex electronic structure of the molecules and the molecular dynamics are the challenges for this mechanism. First measurements will be presented.

[1] M. Wollenhaupt, V. Engel, T. Baumert, Annu. Rev. Phy. Chem. 56, 25 (2005)

[2] M. Wollenhaupt, T. Baumert, J. Photochem. Photobiol. A, 180, 248-255 (2006)

MO 57.3 Do 16:30 Poster A

Ultraschnelle Starkfeldkontrolle an K_2 durch selektive Bevölkerung bekleideter Zustände — •Tim Bayer, Matthias Wollenhaupt, Christian Sarpe-Tudoran und Thomas Baumert — Universität Kassel, Institut für Physik und CINSaT, Heinrich-Plett-Str. 40, D-34132 Kassel, Germany

Die selektive Bevölkerung bekleideter Zustände (SPODS) ist ein elementarer und robuster Mechanismus der kohärenten Quantenkontrolle in intensiven Laserfeldern. In jüngster Vergangenheit wurden zwei Wege zur Realisierung von SPODS durch Pulssequenzen und gechirpte Pulse untersucht und an atomaren Systemen erfolgreich demonstriert. Ferner konnte das Potential dieses Kontrollmechanismus als Anwendung in der Steuerung chemischer Reaktionen anhand von Modellrechnungen am Kalium-Dimer aufgezeigt werden [1]. Nach dem theoretisch vorgeschlagenen Doppelpulsszenario ist es möglich, Populationstransfer via SPODS ultraschnell, selektiv und mit hoher Effizienz zwischen verschiedenen Endkanälen zu schalten.

Der experimentelle Nachweis dieses Szenarios befindet sich derzeit in Arbeit. Wir synchronisieren dazu einen geformten Femtosekundenlaserpuls zur Anregung der neutralen K_2-Dynamik mit einem Nanosekundenlaserpuls zur Endzustandsabfrage, und nutzen die energieaufgelöste Photoelektronenspektroskopie als Methode zum Nachweis der erzielten Endzustandsbesetzung. Es werden vorläufige Ergebnisse präsentiert.

[1] M. Wollenhaupt, T. Baumert, J. Photochem. Photobiol. A **180**, 2006

MO 57.4 Do 16:30 Poster A

Kontrolle der Ausrichtungsdynamik von N_2 — •Christian Horn[1], Rebeca de Nalda[2], Marc Krug[1], Matthias Wollenhaupt[1], Luis Bañares[2] und Thomas Baumert[1] — [1]Universität Kassel, Institut für Physik und CINSaT, Heinrich-Plett-Str. 40, 34132 Kassel, Germany — [2]Dpto. Química Física I, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, Avda. Complutense s/n, 28040 Madrid, Spain

Mit Hilfe von ultrakurzen Laserpulsen kann eine transiente Ausrichtung von Molekülen in der Gasphase erzeugt werden [1]. Wir zeigen, dass die zeitliche Struktur der transienten Ausrichtung mit Hilfe von geformten Laserpulsen kontrolliert werden kann. Dies wird mit Hilfe von Experimenten an N_2 demonstriert. Sowohl die Ergebnisse von "closed-loop" Experimenten, bei denen ein computergesteuerter Algorithmus bestimmte Merkmale der Transiente optimiert, als auch die Ergebnisse von "open-loop" Experimenten werden gezeigt [2]. Der Effekt der Temperatur des Molekülensembles auf das Ausmaß der erzielten Ausrichtung und insbesondere auf die Kontrollmöglichkeiten wird durch numerische Simulationen untersucht [3].

[1] H. Stapelfeldt, T. Seideman, Rev. Mod. Phys. **75**, 543 (2003)

[2] C. Horn, M. Wollenhaupt, M. Krug, T. Baumert, R. de Nalda, L.

Bañares, Phys. Rev. A **75**, 1(R) (2006)
[3] R. de Nalda, C. Horn, M. Wollenhaupt, M. Krug, L. Bañares, T. Baumert, J. Raman Spectrosc. (in print)

MO 57.5 Do 16:30 Poster A

Local control of the quantum dynamics in multiple potential wells. — •Volker Engel, Philipp Marquetand, Stefanie Gräfe, and Daniel Scheidel — Institut für Physikalische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

The driven wave-packet dynamics in potentials exhibiting several potential wells is investigated. Therefore, local control strategies are employed where the control field is constructed from the system's dynamics at any instant of time [1]. It is shown that particles can be moved successively between various potential minima. Furthermore, results are presented which indicate that the intuitive local control scheme allows for the initiation of a clockwise or counter-clockwise rotational motion of a model molecular motor [2]. [1] S. Gräfe, C. Meier, V. Engel, J. Chem. Phys. 122, 184103 (2005). [2] P. Marquetand, S. Gräfe, D. Scheidel, V. Engel, J. Chem. Phys. 124, 054325 (2006).

MO 57.6 Do 16:30 Poster A

Transfer of Vibrational Energy and Quantum Information through Molecular Chains — •Caroline Gollub, Markus Kowalewski, Ulrike Troppmann, and Regina de Vivie-Riedle — LMU Department Chemie, Butenandt-Str. 11, 81377 München, Germany

We are interested in the mechanisms of intramolecular vibrational energy transfer in the context of quantum information transfer and developed different approaches to describe one-dimensional chain molecules. The linear systems consisting of $(C{\equiv}C-)_n$ units are set up with a flexible, modular ansatz based on ab initio quantum chemical data and vibrational eigenfunctions. Additionally, octatetrayne, as a chain molecule, is treated explicitly in a local eigenstate representation. In the modular approach the propagation behavior of the linear, kinetic coupled quantum oscillators of the molecular chains could be studied and dynamical aspects of the vibrational energy transfer were clarified.

These molecular bridge systems offer an innovative possibility to construct quantum networks within our approach of molecular quantum computing [1]. The vibrational qubits are encoded in molecular subunits, linked by the molecular chains. The bridging molecules guarantee the communication between the subunits, which is realized by specially shaped laser pulses, calculated with Optimal Control Theory. Selective quantum state transfer through different quantum channels of the bridging molecules, as well as the entanglement generation and the corresponding mechanisms of the processes are presented.

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

MO 58: Poster: Molecular Dynamics (Theory)

Zeit: Donnerstag 16:30–18:30 Raum: Poster A

MO 58.1 Do 16:30 Poster A

On the geometry dependence of molecular dimer spectra with an application to aggregates of perylene bisimide — •Joachim Seibt[1], Philipp Marquetand[1], Zhijian Chen[2], Volker Dehm[2], Frank Würthner[2], and Volker Engel[1] — [1]Institut für Physikalische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg — [2]Institut für Organische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

We study spectroscopic properties of molecular dimers coupled by dipole-dipole interactions within the framework of time-dependent quantum mechanics. A systematic variation of the dimer geometry allows to establish relationships between the latter and structures in the absorption spectrum. The theoretical model is constructed with the purpose to characterize the changes in absorption and emission properties arising upon aggregation of perylene bisimides. Measured and calculated spectra are compared, thereby addressing the question if a simple exciton model is capable to describe excited state properties of nanoaggregates of these molecules [1].

[1]J. Seibt, P. Marquetand, V. Engel, Z. Chen, V. Dehm, F. Würthner, Chem. Phys. 328, 354 (2006).

MO 58.2 Do 16:30 Poster A

Decoherence of vibrational wave packets — •Martin Schlesinger and Walter Strunz — Theoretische Quantendynamik, Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg

We clarify the effect of rovibrational coupling on the coherence of molecular vibrations [1]. Depending on the temperature chosen we observe a significant suppression of (fractional) revivals in the pump-probe signal [2]. As a measure of coherence we calculate the purity of the vibronic density operator and find a remarkable oscillatory behaviour on the vibrational time scale. Finally we extend our investigations to dimers attached to He nanodroplets [3].

[1] T. Baumert, V. Engel *et. al.*, Chem. Phys. Lett. **191**, 6 (1992)
[2] C. Brif, H. Rabitz *et. al.*, Phys. Rev. A **63**, 063404 (2001)
[3] P. Claas, G. Droppelmann *et. al.*, J. Phys. B (submitted)

MO 59: Poster: Experimental Techniques

Zeit: Donnerstag 16:30–18:30 Raum: Poster A

MO 59.1 Do 16:30 Poster A

Plasma- und Reaktionsdiagnostik in lasergezündeten Verbrennungsvorgängen — •Kurt Iskra und Theo Neger — Institut f. Experimentalphysik, TU Graz, Peteresgasse 16, A-8010 Graz

Der Themenbereich Laserzündung von Motoren wurde in mehreren Aspekten bezüglich der technischen Realisierbarkeit, Optimierung der Parameter und Effizienz auf die motorische Verbrennung untersucht. Die Weiterentwicklung der Lasersysteme zu verbesserter Zündfähigkeit, die Diagnostik der Plasma- und Flammenentwicklung und die Anwendbarkeit auf alternative motorische Brennverfahren waren Ziele weitgehender experimenteller Untersuchungen. Dabei wurde ein breites Spektrum optischer, spektroskopischer und lasermesstechnischer Diagnosemethoden angewandt und weiterentwickelt. Optische Diagnostik von Kurzzeitplasmen, die Laserspektroskopie von Reaktionszwischenprodukten oder in-situ Temperaturmessungen in Hochdruckumgebung durch laserinduzierte Gitter sind Beispiele für die angewandten Methoden. Die Potenziale zur Schadstoffreduktion und technischen Verbesserung des Motorbetriebs wurden erarbeitet.

MO 59.2 Do 16:30 Poster A

Erzeugung schmalbandinger Femtosekunden-Mittelinfrarot-Impulse mittels gechirpter Nahinfrarot-Impulse — •Karin Haiser, Florian Koller, Markus Huber, Tobias Schrader, Wolfgang Schreier und Wolfgang Zinth — Lehrstuhl für BioMolekulare Optik, Department für Physik der Ludwig-Maximilians-Universität, Öttingenstr. 67, 80538 München

Für die Aufnahme von 2D-Infrarotspektren in Doppelresonanzexperimenten sind spektral schmale Anregungsimpulse im Bereich von 10 bis 30 cm^{-1} erforderlich, um die für polyatomare Moleküle in Lösungen benötigte Auflösung zu erreichen. In IR-Anreg-IR-Abtast-Experimenten wird der Anregungsimpuls im Mittelinfraroten typischerweise durch eine Differenzfrequenzmischung (DFM) von zwei nahinfraroten Femtosekunden-Impulsen in einem Kristall erzeugt. Hier treten i.A. spektrale Breiten von mehr als 100 cm^{-1} auf. Mittels Chirpen der beiden Nahinfrarot-Impulse durch Integration von Si-Prismen-Expandern in den Strahlengang kann erreicht werden, dass bei der Differenzfrequenzmischung schmalbandiges Licht erzeugt wird.

Mit dieser neuen Methode lassen sich IR-Pump-Impulse mit spektralen Breiten von wenigen 10 cm^{-1} mit hoher Konversion erzeugen. Durch Variation der Verzögerung der Signal- und Idler-Impulse zuein-

ander lässt sich zudem die Frequenz des Mittelinfrarot-Impulses sehr einfach über ca. 100 cm^{-1} durchstimmen.

MO 59.3 Do 16:30 Poster A

Aufbau eines Pump-Probe-Experiments für transiente IR-Spektroskopie auf der ns-Zeitskala — •Michael Brandl, Nadja Regner, Tobias Schrader und Wolfgang Zinth — Lehrstuhl für BioMolekulare Optik, Department für Physik, Ludwig-Maximilians-Universität München, Oettingenstr. 67, 80538 München

Dynamische Prozesse in Molekülen decken einen Zeitbereich von wenigen fs (z.B. H-Brückendynamiken) bis ms (z.B. Faltungsdynamiken in Proteinen) ab. Pump-Probe-Experimente können mit Hilfe von ultrakurzen Lichtimpulsen und variablen optischen Wegen Abläufe auf der fs- und ps-Skala aufnehmen. Längere Verzögerungszeiten im ns- bis μs-Bereich führen mit dieser Methode jedoch zu erheblich Problemen mechanischer (100 ns = 30 m opt. Weglänge) und optischer (Strahlaufweitung) Natur. Für diesen Zeitbereich lassen sich jedoch elektronische Verzögerungen realisieren. In unserem Aufbau wurde dazu ein vorhandenes mit einer Wiederholrate von 1 kHz betriebene Ti:Sa-Lasersystem mit einem ns-Laser synchronisiert. Die Kombination beider Ansätze ermöglicht die Verfolgung ultrakurzer Moleküldynamiken von wenigen fs bis etwa 3 ns mit Hilfe des Ti:Sa-Lasersystems. Der Bereich von 3 ns bis zu vielen μs kann dann mit den zwei synchronisierten Lasern mit einer Auflösung von 1 ns (limitiert durch die Impulslänge) gemessen werden.

MO 61: Quantum Control I

Zeit: Freitag 10:30–12:30 Raum: 6F

MO 61.1 Fr 10:30 6F

Excitation of C_{60} with Temporally Shaped Laser Pulses: Coherent Heating of Nuclear Motion — •Claus Peter Schulz, Ihar Shchatsinin, Tim Laarmann, Nickolai Zhavoronkov, and Ingolf Volker Hertel — Max Born Institute, Max-Born-Str. 2a, 12489 Berlin-Adlershof, Germany

Femtosecond laser pulses tailored with closed-loop, optimal control feedback were used to optimise the C_2 evaporation from C_{60} [1]. A characteristic pulse sequence results in significant enhancement of the C_{50}^+ yield, a typical fragment of vibrationally hot C_{60}, in comparison with the response to a single pulse of the same energy and overall width. The separation between subsequent pulses is close to the vibrational period of the radial symmetric $a_g(1)$ breathing mode. In a two-colour pump-probe experiment similar modulations were observed in the ion signal of multiply charges fragments. The observed period (80-127 fs) of this oscillation depends on the degree of ionisation and the deposited energy. Comparison with TDDFT calculations indicates that the shaped laser pulse excite giants oscillations in C_{60}, which prevails for several cycles.

[1] T. Laarmann, I. Shchatsinin, A. Stalmashonak, M. Boyle, N. Zhavoronkov, J. Handt, R. Schmidt, C. P. Schulz, and I.V. Hertel, Physical Review Letters, in press (2006)

MO 61.2 Fr 10:45 6F

Laserinduced breathing mode in highly excited C_{60} — •Jan Handt[1] and Rüdiger Schmidt[2] — [1]Max-Planck-Institut für Physik komplexer Systeme, Nöthnitzer Strasse 38, D-01187 Dresden — [2]Institut für Theoretische Physik, Technische Universität Dresden, D-01062 Dresden

We present, a theoretical study of the excitation of C_{60} by strong laser pulses. We use the so-called nonadiabatic quantum molecular dynamics (NA-QMD) which combines self-consistently the electron dynamics treated with time-dependent density functional theory (td-DFT) and classical molecular dynamics. Exciting the molecule via the t_{1g} resonance our calculations show a strong multielectron excitation of C_{60}. Surprisingly most of the vibrational energy is stored in the $a_g(1)$ breathing mode. The period of the breathing mode depends on the deposited energy. We show, that oscillations observed in pump-probe and optimal-control experiments are due to this effect [1]. [1] T. Laarmann, I. Shchatsinin, A. Stalmashonak, M. Boyle, N. Zhavoronkov, J. Handt, R. Schmidt, C. P. Schulz, and I.V. Hertel, Physical Review Letters, in press (2006)

MO 61.3 Fr 11:00 6F

Optimale Kontrolle von laserinduzierten Reaktionen von H_2 mit CO auf einer Pd(100) — •Daniel Wolpert[1], Patrick Nuernberger[1], Horst Weiss[2] und Gustav Gerber[1] — [1]Physikalisches Institut, Universität Würzburg, Am Hubland, — [2]BASF AG, Polymer Research Division, 67056 Ludwigshafen, Germany

Wir untersuchen die Reaktion von H_2 und CO Molekülen auf einer Pd(100) Einkristalloberfläche mit Femtosekunden-Laserimpulsen. Mittels Flugzeitmassenspektroskopie werden verschiedene Produktmoleküle, darunter auch solche (z.B. CH_3^+), bei deren Bildung mindestens drei Reaktionspartner mit der Oberfläche und dem Laserfeld wechselwirken müssen, beobachtet. Durch die Anwendung von optimal geformten Femtosekunden-Laserimpulsen können die Verhältnisse der entstehenden Produktionen gezielt beeinflusst werden. Im Gegensatz zu früheren Quantenkontrollexperimenten, in denen Bindungen in Molekülen selektiv gebrochen wurden, wird hier die Bildung von Molekülbindungen kontrolliert.

MO 61.4 Fr 11:15 6F

Coherent Control despite a dominant spectral Continuum: — •Heide Ibrahim[1], Mónika Héjjas[1], Mizuho Fushitani[2], Markus Gühr[3], and Nikolaus Schwentner[1] — [1]FU Berlin, Institut für Experimentalphysik, Arnimallee 14, 14195 Berlin — [2]Institute for Molecular Science, Okazaki, Aichi 444-8585, Japan — [3]Stanford PULSE Center, Varian Physics Bldg., 382 Via Pueblo Mall, Stanford CA 94305-4060, USA

The interaction strength of a vibrational mode with a multidimensional (crystalline) environment is reflected in frequency domain spectroscopy in the lineshape. Weak coupling leads to sharp zero-phononlines (ZPL) which represent an exclusive chromophore vibrational excitation. Phonon side bands (PSB) display the simultaneous excitation of bath modes which merge to a continuum with increasing strength. Concerning coherent control of molecular dynamics it is desirable to generate analoguos weakly and strongly coupled vibrational wave packets composed of ZPL or PSB respectively by appropriate femtosecond pulse sequences. The X-A and X-B transitions of Br_2 in an Ar matrix provide these properties and are used to develop the means to achieve this separation with phase locked pulses. Firstly we show that the powerful A continuum and the faint B progression can be sorted out by either state-selective fluorescence or an additional probe step. Secondly we illustrate how variably coupled wave packets are generated by optimising timing and phases of pulse sequences. Pros and cons of sequence generation with spatial light modulators or interferometers are analysed based on a Fouriertransformation.

MO 61.5 Fr 11:30 6F

Analyse von Mechanismen der Quantenkontrolle durch farbige Femtosekunden-Doppelimpulse — Gerhard Vogt, Patrick Nuernberger, Reimer Selle, •Frank Dimler, Tobias Brixner und Gustav Gerber — Physikalisches Institut, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

Die einer adaptiven Quantenkontrolle mit Femtosekunden-Laserimpulsen zugrunde liegenden Mechanismen können mit Hilfe von sogenannten Fitnesslandkarten, die nur von einer beschränkten Anzahl von Impulsformparametern abhängen, gefunden werden [1]. Bei der Fitness handelt es sich hierbei beispielsweise um die Effizienz einer Photoreaktion.

In einem ersten Experiment werden farbige Femtosekunden-Doppelimpulse verwendet, um eine solche Fitness als Funktion der zeitlichen Separation und der relativen Amplitude der beiden Laserimpulse aufzunehmen. Der Vergleich mit den Ergebnissen einer freien Optimierung zeigt die Übereinstimmung mit der Fitnesskarte.

In einem weiteren Experiment wird geklärt, ob die Anregungseffizienz des Laserfarbstoffes IR140 bei linear gechirpten Laserimpulsen äquivalent ist zur Anregung mit farbigen Doppelimpulsen bei entsprechendem Zeit- und Frequenzabstand.

[1] G. Vogt et al., Phys. Rev. A **74,** 033413 (2006)

MO 61.6 Fr 11:45 6F

Selective bond breaking in model dipeptides with temporally shaped laser pulses — •Tim Laarmann, Ihar Shchatsinin, Nick Zhavoronkov, Claus Peter Schulz, and Ingolf Volker Hertel — Max Born Institute, Max-Born-Str. 2A, 12489 Berlin

The control of photophysical processes with judiciously tailored femtosecond laser pulses is a cutting edge topic in modern laser science and might pave the way to optically controlled organic chemistry [1]. In this contribution we report on pulse-shaping experiments using closed-loop, optimal control feedback for selective bond breaking in Ac-Phe-NHMe. This molecule contains a -CO-NH-CHR-CO- moiety, the key structural element of peptides. Moreover, due to the two amino groups this system can be regarded as a model dipeptide. Perspectives for "laser-induced protein sequencing (LIPS)" using temporally shaped laser pulses will be discussed.

[1] T. Laarmann, I. Shchatsinin, A. Stalmashonak, M. Boyle, N. Zhavoronkov, J. Handt, R. Schmidt, C. P. Schulz, and I.V. Hertel, Physical Review Letters, in press (2006)

MO 61.7 Fr 12:00 6F

Quantum Information Transfer through Molecular Chains — •Caroline Gollub, Ulrike Troppmann, and Regina de Vivie-Riedle — LMU Department Chemie, Butenandt-Str. 11, 81377 München, Germany

Molecular bridge systems consisting of $(C{\equiv}C-)_n$ units, such as octatetrayne, offer an innovative possibility to construct quantum networks, within our approach of molecular quantum computing [1].

The vibrational qubits are encoded in selected normal modes of molecular subunits. These multiple nodes are connected by molecular chains to larger quantum registers. Ultrashort, shaped laser pulses, act as quantum gates on the multi-qubit systems. Independent control of the nodes is possible. The bridging molecules represent the units, essential for quantum information transfer. The communication between the qubit systems is realized by specially shaped, ultrashort laser pulses, calculated with Optimal Control Theory. In this context we present shaped pulses inducing selective quantum state transfer through different quantum channels of the bridging molecules. Additionally, the generation of inter-node superpositions has to be required for quantum multicomputers and we demonstrate the implemenation of entanglement generation in our approach of scalable molecular quantum computing with vibrational qubits.

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

MO 61.8 Fr 12:15 6F

Single-beam Heterodyne CARS for Sensitive Chemically Selective Microscopy — •Bernhard von Vacano, Tiago Buckup, and Marcus Motzkus — Physikalische Chemie, Philipps-Universität Marburg, D-35032 Marburg, Germany

With shaped femtosecond laser pulses, coherent anti-Stokes Raman-scattering (CARS) microspectroscopy can be accomplished in a straight-forward single-beam approach. To increase the sensitivity, we introduce interferometric detection in a very simple experimental extension: in addition to the optical fields driving the CARS process, a controllable local oscillator is derived by pulse-shaping of a single femtosecond laser beam. The heterodyne detected signal can be amplified by more than three orders of magnitude and shows linear concentration dependence. Like this, the sensitivity of chemically selective CARS detection can be increased dramatically, without adding complexity to the single-beam setup. As an example, we show sensitive and chemically selective detection of down to 8×10^6 analyte molecules.

MO 62: Collisions with electrons and ions (gemeinsam mit A)

Zeit: Freitag 10:30–12:15 Raum: 5M

Hauptvortrag MO 62.1 Fr 10:30 5M

Angular analysis of x–ray emission from excited ionic states with unresolved fine structure — •Andrey Surzhykov[1], Ulrich Jentschura[1], Thomas Stöhlker[2], and Stephan Fritzsche[3] — [1]Max–Planck–Institut für Kernphysik, Heidelberg — [2]Gesellschaft für Schwerionenforschung (GSI), Darmstadt — [3]Universität Kassel

At storage rings, the various processes occurring in relativistic collisions of heavy ions with atomic or electronic targets may result in the production of excited ionic states. The subsequent decay of these excited states leads to emission of one (or several) photons until the ground state is reached. The angular analysis of such a characteristic x-ray emission is a valuable tool for studying the structure and dynamics of highly-charged ions. Quite often, however, the decay photons from two (or more) excited ionic states cannot be distinguished by x-ray detectors and, hence, only "averaged" angular information is available from experiment. In this contribution, we present a theoretical study for the angular distributions of the unresolved characteristic lines and argue that even the "averaged" emission patterns may help us to understand the population–and–decay of high-Z ions. As an example, we present our calculations for the $K\alpha_1$ decay of the excited $1s2p_{3/2}J = 1, 2$ states of the helium–like uranium ions U^{90+} produced in the course of two different population processes: (i) the radiative electron capture and (ii) the Coulomb excitation. Experiments concerning these processes have recently been performed at GSI in Darmstadt, and the angular distributions observed have been found to be inconsistent with the predictions of a one–particle model.

MO 62.2 Fr 11:00 5M

Photon angular distribution and nuclear-state alignment in nuclear excitation by electron capture — •Adriana Pálffy[1], Zoltán Harman[1], Andrey Surzhykov[1], Ulrich D. Jentschura[1], and Werner Scheid[2] — [1]Max-Planck-Institut für Kernphysik, Heidelberg — [2]Institut für Theoretische Physik, Giessen

We investigate the resonant process of nuclear excitation by electron capture (NEEC), in which a free electron is captured into a bound atomic shell with the simultaneous excitation of the nucleus. Partly due to the radiative recombination (RR) background, NEEC has not been observed experimentally yet. In Ref. [1,2] total cross sections for NEEC followed by the radiative decay of the nucleus are presented. The measurement of the angular distribution of the emitted photons in the recombination process offers an useful method of discerning NEEC from RR. With the help of a density matrix formalism the angular distribution of the photons emitted in the radiative decay of the nucleus is derived. We present the anisotropy parameters and the angular distribution of the photons emitted in a radiative E2 decay of the nuclear state for the capture of the electron into the K shell of several bare ions. The angular pattern of the photon emission for NEEC can serve as a signature for the occurrence of the process.

[1] A. Palffy, W. Scheid and Z. Harman, Phys. Rev. A 73, 012715 (2006)

[2] A. Palffy, Z. Harman and W. Scheid, Phys. Rev. A 74, in press (2006)

MO 62.3 Fr 11:15 5M

A photoemission source for experiments on electron impact ionization of atoms and molecules — •Vladimir Borovik, Toshiyasu Ichioka, Claus Dieter Schröter, Alexander Dorn, and Joachim Ullrich — Max-Planck-Institut für Kernphysik, Saupfercheckweg 1, D-67119 Heidelberg, Germany

The investigation of single and multiple ionization of atoms by electron impact allows insight into the dynamics of fundamental few-body quantum systems. In the past we have performed these studies combining a standard thermo-cathode electron beam source with a Reaction Microscope (see, e.g., Dürr et al., PRL 96, 243202). In future we aim to improve the electron beam quality concerning the energy definition and timing structure. We therefore have built a photoemission source based on a semiconductor cathode with negative electron affinity (NEA). The design, the preparation procedure of the GaAs crystal and the resulting beam properties will be presented.

MO 62.4 Fr 11:30 5M

Kinematically complete experiments on ground-state dissociation of H_2 molecules by electron impact — •Arne Senftleben[1], Nicole Haag[2], Alexander Dorn[1], Martin Dürr[1], and Joachim Ullrich[1] — [1]Max-Planck-Institut für Kernphysik, 69117 Heidelberg, Germany — [2]Stockholms universitet, 10691 Stockholm, Sweden

Collisions of molecular hydrogen with 210 eV electrons have been studied kinematically complete, allowing to examine the collision dynamics as detailed as possible. Besides pure ionisation the so-called ground state dissociation channel (GSD) has been investigated where the ionised molecules are excited to the vibrational continuum and subsequently dissociate. This allows to extract the orientation of the molecular axis at the time of the collision. Using a multi-electron recoil-ion momentum spectrometer (reaction microscope) all charged reaction products were detected over a large solid angle. With this technique the GSD of H_2 could be examined in a kinematically complete measurement for the first time. Differential cross-sections were obtained as a function of molecular alignment with respect to the projectile beam.

MO 62.5 Fr 11:45 5M

Untersuchung der Endzustände bei der dissoziativen Rekombination von CF^+: Ein verbesserter Detektor zur dreidimensionalen Multi-Fragment-Abbildung — •Mario Mendes[1], Steffen Novotny[1], Oldrich Novotny[1], Iftach Nevo[2], Henrik Buhr[1], Dirk Schwalm[1,2], Daniel Zajfman[2] und Andreas Wolf[1] — [1]Max-Planck-Institut für Kernphysik, Heidelberg — [2]Weizmann Institute of Science, Rehovot, Israel

Zur Untersuchung der dissoziativen Rekombination (DR) wird am Testspeicherring (TSR) des Max-Planck-Instituts für Kernphysik in Heidelberg ein Detektor zur Abbildung der beim DR-Prozess entstehenden neutralen Fragmente verwendet, welcher für eine prinzipiell nicht limitierte Anzahl innerhalb weniger Nanosekunden auftreffender Fragmente Positionen und Auftreffzeiten registriert [1]. Wesentlicher Bestandteil dieses Detektors ist ein System zweier CCD-Kameras, von denen eine mit Hilfe eines schnell schaltbaren Verstärkers geschlossen werden kann. Die Zeitauflösung des Detektors hängt dabei von der Abschaltzeit ab. Diese Abhängigkeit wurde eingehend untersucht und im Rahmen einer konstruktiven Verbesserung des Detektors ausgenutzt. Die Endzustände bei der dissoziativen Rekombination von CF^+ und ihre Winkelverteilungen konnten aus dreidimensionalen Daten bei verschiedenen Elektronenstoßenergien bestimmt werden. Von drei energetisch möglichen Endzuständen werden bei Stoßenergie Null nur zwei beobachtet. Bei hohen Energien variiert das Verzweigungsverhältnis der Endzustände stark.

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

MO 62.6 Fr 12:00 5M

Kinematisch vollständige Untersuchung von Zwei-Zentren Effekten bei der simultanen Ionisation von Projektil und Target in H^- - He Stößen — •Thomas Ferger[1], Daniel Fischer[1,2], Michael Schulz[3], Robert Moshammer[1], Alexander B. Voitkiv[1], Bennaceur Najjari[1] und Joachim Ullrich[1] — [1]MPIK-Heidelberg, Germany — [2]Stockholm University, Sweden — [3]UMR Missouri, USA

In diesem Experiment wurde die simultane Ionisation von Projektil und Target in Stößen von H^- mit He bei einer Projektilenergie von 200 keV mit Hilfe eines "Reaktions Mikroskops"kinematisch vollständig vermessen. Betrachtet man das schwach gebundenen Elektron des H^- Projektils (Ionisationspot. = 0,75 eV) als ein quasi freies Elektron so erwartet man, dass die gemessenen vollständig differentiellen Wirkungsquerschnitte (FDCS) für die Ionisation von He vergleichbar sind mit einer Elektronenstoßionisation (e,2e) durch ein freies Elektron bei der entsprechenden Projektilgeschwindigkeit (E_e = 109 eV). Durch die Anwesenheit des Projektilkerns kann zusätzlich der Einfluss des Zwei-Zentren Coulomb-Potentials untersucht werden. Neben der Elektron-Elektron Wechselwirkung treten weitere Beiträge höherer Ordnung auf, die insbesondere in den FDCS der Projektilionisation deutlich werden. Anhand von so genannten Dalitz-Plots wird versucht dieses Vier-Körper Problem auf einfachere Wechselwirkungen zu reduzieren.

MO 63: Spectroscopy in He-droplets / Ultracold Molecules I (gemeinsam mit Q)

Zeit: Freitag 10:30–12:45 Raum: 6B

Fachvortrag MO 63.1 Fr 10:30 6B

Magnetic dichroism of alkali atoms and molecules on the surface of helium nanodroplets — Johann Nagl, Gerald Auböck, Carlo Callegari, and •Wolfgang E. Ernst — Institute of Experimental Physics, TU Graz, Petersgasse 16, A-8010 Graz, Austria

We measured laser induced fluorescence spectra of K and Rb atoms, dimers and trimers, on the surface of superfluid helium droplets, with and without a moderately strong external magnetic field ($\approx$ 3 kG). Atomic spectra (D lines) are saturated with a few hundred mW of laser power. In a magnetic field, and under saturation, we observe a greater signal for linear polarization but no difference between the two states of (circular) polarization of the exciting laser. We take this as evidence that the two spin sublevels of the ground-state alkali atoms are equipopulated, despite a Zeeman splitting comparable in magnitude to kT (at the temperature of the droplet, $T = 0.38$ K). We estimate that the rate of spin relaxation induced by the droplet must be < 1000/s. We thus demonstrate that by selective depletion it is possible to create a beam of He droplets doped with spin-polarized alkali atoms.

Measurements on triplet dimers do show magnetic circular dichroism, indicating that, unlike atoms, molecules do undergo fast spin relaxation and do thermalize to the temperature of the droplet.

MO 63.2 Fr 11:00 6B

Simulation der Dotierung von Heliumnanotröpfchen mit Alkaliatomen — •Oliver Bünermann und Frank Stienkemeier — Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg

Heliumnanotröpfchen haben die Eigenschaft jegliche Teilchen über inelastische Stöße aufzusammeln. Dies kann zum Dotieren der Tröpfchen ausgenutzt werden: In einer Streuzelle wird ein entsprechender Dampfdruck des zu untersuchenden Materials eingestellt, die Tröpfchen passieren die Zelle und sammeln je nach Dampfdruck eine bestimmte Anzahl von Teilchen auf. Die Wahrscheinlichkeit $P_k(p)$, dass ein Tröpfchen k Teilchen aufgesammelt hat, ist poissonverteilt. Experimentell ermöglicht die Aufnahme von Dotierungskurven (Signal in Abhängigkeit vom Dampfdruck) einer gefundenen Absorbtion eine Komplexgröße zuzuordnen.

Im Experiment zeigen sich allerdings zum Teil starke Abweichung der Dotierungswahrscheinlichkeit von der Poissonverteilung. Insbesondere bei Alkaliatomen, -molekülen und -clustern kann man nicht mehr von einer Poissonverteilung sprechen. Eine Simulation des Dotierungsprozesses von Alkaliatomen wurde durchgeführt, die die Größenverteilung der Tröpfchen, die Tröpfchenschrumpfung nach er Dotierung, die Desorption der dotierten Komplexe und den Impuls Eintrag auf die Tröpfchen berücksichtigt. Im Rahmen der Simulation erhält man eine gute qualitative Übereinstimmung mit dem Experiment. Es zeigt sich, das die Wahl der Tröpfchenbedingungen einen entscheidenden Einfluss auf die Form der Dotierungskurven hat.

MO 63.3 Fr 11:15 6B

Aggregation von HCl in Heliumnanotröpfchen — •Markus Ortlieb, Anja Metzelthin, Melanie Letzner und Martina Havenith — Physikalische Chemie II, Ruhr-Universität Bochum, Universitätstr. 150, D-44780 Bochum

Wir untersuchen die Aggregation von HCl bei ultrakalten Temperaturen in Heliumnanotröpfchen im Bereich von 2820 bis 2940 cm^{-1}. Die Messungen wurden mit einem leistungsstarken IR-OPO (cw: 2,9 W) durchgeführt. Anhand der Druckabhängigkeit der Signalstärken konnten die Linien dem HCl Monomer, Dimer und Trimer zugeordnet werden. Dabei zeigte sich, dass die Frequenzen des Trimers auf die Ausbildung einer linearen Kette aus HCl hinweisen.

Weiterhin untersuchen wir das IR-Spektrum des Radikals NO in Heliumtröpfchen mit unserem Bleisalzdiodenlaser (Auflösung: 0,001 cm^{-1}). Der $^2\Pi_{1/2}$ R(1/2) Übergang des $^{15}N^{18}O$ Isotops konnte bei 1796,39 cm^{-1} gemessen werden, was einer Verschiebung von 0,12 cm^{-1} im Vergleich zur Gasphase entspricht.

MO 63.4 Fr 11:30 6B

Spectroscopy of free radicals and radical containing entrance-channel complexes in superfluid helium nanodroplets — •Jochen Küpper[1,2], Jeremy M. Merritt[2], and Roger E. Miller[2] — [1]Fritz-Haber-Institut der MPG, Faradayweg 4-6, 14195 Berlin — [2]University of North Carolina, Department of Chemistry, Chapel Hill, NC 27599, USA

The unique properties of superfluid helium nanodroplets, namely their low temperature (0.4 K) and fast cooling rates ($\sim 10^{16}$ K s^{-1}), provide novel opportunities for the formation and high-resolution study of metastable structures or molecular complexes containing free radicals.

We discuss methods for the production of radicals and their applicability for embedding the radicals in helium nanodroplets. The spectroscopy of free radicals (i. e. C_3H_3) and of radical containing entrance-channel complexes, for example X$\cdots$HY (X=Cl, Br, I, CH_3; Y=F, CN), embedded in helium nano-droplets is detailed. The observed complexes provide new information on the potential energy surfaces of several fundamental chemical reactions and on the intermolecular interactions present in open-shell systems. Prospects for further experiments of radicals embedded in helium droplets are discussed.

MO 63.5 Fr 11:45 6B

Sub-megaherz infrared spectroscopy of trapped HD^+ ions at millikelvin temperatures — •Jeroen Koelemeij, Bernhard Roth, Andreas Wicht, Ingo Ernsting, and Stephan Schiller — Institut für Experimentalphysik, Universität Düsseldorf

We have performed an absolute frequency measurement of the $(v' = 4, J' = 3) \leftarrow (v = 0, J = 2)$ overtone transition at 1395 nm in the molecular HD^+ ion with sub-megaherz accuracy. Trapped HD^+ ions are sympathetically cooled to millekelvin temperatures by storing them together with Be^+ ions, which are laser cooled to ~ 10 mK using near-resonant 313 nm light. Vibrational overtone spectroscopy at 1395 nm is done using $(1 + 1')$ resonance-enhanced multiphoton dissociation (REMPD), where a second photon at 266 nm selectively dissociates the HD^+ ions in $v' = 4$. The loss of HD^+ ions due to the REMPD process manifests itself as a change in the 313 nm Be^+ fluorescence when the motion of the HD^+ ions is resonantly driven by an ac electric field. The 1395 nm probe laser is a narrowband grating-enhanced diode laser with resonant optical feedback, which is locked to a femtosecond frequency comb. The comb is stabilized to a hydrogen maser which is referenced to GPS for long term stability. This allows tuning and measurement of the 1395 nm laser frequency with an accuracy better than 10 kHz. The 0.5 MHz uncertainty in our final result is due to measurement noise, Doppler broadening and, to a lesser extent, systematic uncertainties associated with external fields in the ion trap, and uncertainties in the *ab initio* data used for the spectral fit model.

MO 63.6 Fr 12:00 6B

Buffer-gas cooling of CrH and MgH in a cryogenic magnetic trap for paramagnetic molecules — •Michael Stoll[1], Tim Steimle[2], Gerard Meijer[1], and Achim Peters[3] — [1]Fritz-Haber-Institut der Max-Planck-Gesellschaft — [2]Department of Chemistry and Biochemistry, Arizona State University — [3]Humboldt Universität zu Berlin, Institut für Physik

The buffer gas loading and subsequent magnetic trapping of neutral molecules is a powerful tool for it can provide samples of cold molecules with very high densities. We report on the buffer-gas cooling of CrH and MnH radicals to a temperature of below 1 K, using a dilution refrigerator. We also present data on the first attempts to trap CrH and discuss inelastic scattering with the Helium background gas as a possible loss mechanism preventing effective trapping.

Further experiments using CrD, MnH and MnD should give additional information on the exact role of inelastic scattering processes. First estimations indicate that trapping of MnH should in principle be feasible in our current setup, whereas trapping of CrH would require substantial modifications to our cryogenic system.

MO 63.7 Fr 12:15 6B

UV photodissociation studies of polyatomic molecular ions at milli-Kelvin temperatures — •David Offenberg, Chaobo Zhang, Bernhard Roth, and Stephan Schiller — Institut für Experimentalphysik, Heinrich-Heine-Universität Düsseldorf

Photodissociation spectroscopy is a commonly used tool to investigate molecular properties. The spectral resolution can be enhanced by reducing the molecules' thermal energy [1], as recently demonstrated on *diatomic* molecular ions [2]. Here, we present our initial advances towards photodissociation spectroscopy of *polyatomic* molecules.

As a first model system we use translationally cooled, singly protonated molecules of Glycyrrhetinic Acid (GA) − a biomolecule of mass 471 amu consisting of 80 atoms. In our apparatus, the molecular ions are generated by an electrospray ionization source, transferred to and stored in a radio-frequency trap together with laser-cooled barium ions. Due to their Coulomb interaction with the atomic coolant, they cool down from ambient temperature to the hundred milli-Kelvin range and can be kept and investigated under these low-temperature and nearly collisionless conditions for more than one hour [3]. We have measured the photodissociation rate of GA ions using a single-frequency cw-laser at 266 nm. In further studies we plan to investigate the feasibility of resonance enhanced two-photon dissociation with additional tunable IR lasers.

[1] O. Boyarkin et al., J. Am. Chem. Soc. 128, 2816 − 2817 (2006)
[2] B. Roth et al., Phys. Rev. A 74, 040501(R) (2006)
[3] A. Ostendorf et al., Phys. Rev. Lett. 97, 243005 (2006)

MO 63.8 Fr 12:30 6B

Preparation of single molecular ions for time resolved electron diffraction — •Steffen Kahra, Günther Leschhorn, Axel Friedenauer, Hector Schmitz, Ernst Fill, and Tobias Schätz — Max-Planck-Institut für Quantenoptik, 85741 Garching

We present a scheme for the preparation of isolated single molecular ions. The ions will be confined in a linear Paul-trap. This allows besides for excellent spacial positioning with accuracy of only a few micrometers also for application of common sympathetic cooling techniques. Since the ions are accessible to manipulation by laser and electron beams, for example, a wide range of experimental opportunities arises. Investigation of one of the most intriguing realms in nature comes into reach when we combine our tool with the recent and foreseeable developments made in the field of short electron pulse generation. Doing electron or X-ray diffraction (100 fs) on isolated species in a time resolved manner, might provide us with direct information about the electronic motion inside the charged molecule. Hence, observing the molecule by means of diffraction and taking spectroscopic knowledge into account is expected to help us understand how the dynamic structure of an excited molecule on the few femtosecond timescale really evolves.

Supported by: IMPRS, MAP, MPG

MO 64: Quantum Control II

Zeit: Freitag 14:00–16:00 Raum: 6F

MO 64.1 Fr 14:00 6F

Darstellung ultrakurzer Laserpulse mittels von Neumann-Repräsentation — •Susanne Fechner[1], Frank Dimler[1], Florin Boariu[1], Tobias Brixner[1], David Tannor[2] und Gustav Gerber[1] — [1]Physikalisches Institut, Universität Würzburg, Am Hubland, 97070 Würzburg — [2]Deptartment of Chemical Physics, Weizmann Institute of Science, 76100 Rehovot, Israel

Im Gegensatz zur üblichen Darstellung des elektrischen Feldes im Frequenz- oder im Zeitraum bieten Phasenraumdarstellungen die Möglichkeit, die spektralen und zeitlichen Eigenschaften ultrakurzer Laserimpulse simulatan und auf intuitive Weise zu erfassen. Prominente Beispiele solcher Joint Time Frequency-Darstellungen sind die Wigner- und die Husimi-Repräsentation, die breite Anwendung in der aktuellen Forschung finden.

Die von uns untersuchte, auf von Neumann zurückgehende Phasenraumdarstellung erlaubt im Gegensatz zu den üblicherweise verwendeten eine vollständige Rekonstruktion des elektrischen Feldes bei gleichzeitigem Erhalt der intuitiven Interpretierbarkeit. Die in der von Neumann-Repräsentation verwendeten Basisfunktion sind um einen bestimmten Frequenz-Zeitpunkt zentrierte, gaussförmige Impulse, aus denen das elektrische Feld konstruiert werden kann.

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

MO 64.2 Fr 14:15 6F

The effect of multipulse envelope modulation by phase sha-

ping on Pump-Probe spectroscopy — •Tiago Buckup[1], Jürgen Hauer[1], Carles Serrat[2] und Marcus Motzkus[1] — [1]Physikalische Chemie, Philipps Universität Marburg, D-35032 Marburg, Germany — [2]Departament de Fisica, Universitat Politècnica de Catalunya, 08222 Terrassa, Spain

The manipulation of wave packet phenomena plays a significant role in the field of coherent control, with applications reaching from atomic systems to biomolecules. Wave packet control is often achieved with sequences of phase locked pulses, usually generated with sinusoidal modulation in spatial light modulators. In this context, the period of the sinusoidal modulation defines the subpulse spacing and allows the filtering as well as the amplitude enhancement of molecular vibrations. In this work, we discuss the effect of the phase of the sinusoidal modulation on the envelope of the multipulse sequence and its consequences on pump-probe spectroscopy, particularly near zero delay between pump and probe pulses. We show that the multipulse envelope modulation stems from interference between the subpulses and is dependent on the phase of the individual subpulses. The effect is quantified in terms of the spectrum deviation from a Gaussian shape and is simulated numerically for different spectral shapes. Finally, the multipulse envelope modulation is simulated and measured in ultrafast transient absorption and four-wave mixing.

MO 64.3 Fr 14:30 6F

Selektive Bevölkerung bekleideter Zustände: Vermessung von Kontrolllandschaften durch „orthogonale“ Pulsparametrisierung — •Tim Bayer, Matthias Wollenhaupt, Christian Sarpe-Tudoran, Jutta Mildner und Thomas Baumert — Universität Kassel, Institut für Physik und CINSaT, Heinrich-Plett-Str. 40, D-34132 Kassel, Germany

Die selektive Bevölkerung bekleideter Zustände (SPODS) ist der Schlüssel zur Kontrolle von Quantensystemen in intensiven Laserfeldern. Um ein Verständnis grundlegender Mechanismen der SPODS-Realisierung zu entwickeln, untersuchen wir die *resonante* Starkfeldanregung des $4s \leftarrow 4p$ Übergangs in Kalium durch geformte Femtosekunden-Laserpulse. Photoelektronenspektren, gewonnen aus der simultan ablaufenden Ionisation der K-Atome, dienen als Nachweis der transienten Wechselwirkungsdynamik. Es zeigt sich, dass kontinuierlich veränderliche zeitliche Phasen ebenso wie diskrete Phasensprünge genutzt werden können, um Kontrolle auf die Besetzung der bekleideten Zustände auszuüben. Die damit verbundenen Pulsformen bzw. Kontrollmechanismen sind allerdings grundlegend verschieden, sodass die zugehörigen Kontrollparameter als „orthogonal“ aufgefasst werden können. Eine Pulsparametrisierung nach diesen beiden Mechanismen führt daher zu einer *sinnvollen* Reduzierung des Suchraumes und erlaubt es, dessen Kontrolltopologie zu vermessen. Wir präsentieren SPODS-Kontrolllandschaften, die auf der Grundlage einer solchen Parametrisierung gemessen wurden.

MO 64.4 Fr 14:45 6F

Characteristics of wavepacket evolution from quantum control landscapes — •Philipp Marquetand[1], Patrick Nürnberger[2], Gerhard Vogt[2], Tobias Brixner[2], and Volker Engel[1] — [1]Institut für Physikalische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg — [2]Physikalisches Institut , Universität Würzburg, Am Hubland, 97074 Würzburg

We are using shaped dump pulses to map the evolution of a wavepacket in an excited state. By systematic variation of selected pulse parameters, we monitor the efficiency for a transition to the groundstate. From the resulting two-dimensional fitness landscapes information on the wavepacket shape and the system under study can be deduced. Results from simplified model calculations are presented and first experiments on the retinal photoisomerization reaction in bacteriorhodopsin have been performed.

MO 64.5 Fr 15:00 6F

Calculation of 2D spectra of the FMO complex — •Ben Brüggemann[1,2], Pär Kjellberg[1], and Tonu Pullerits[1] — [1]Chemical Physics, Lund University, Sweden — [2]Institut für Physik, Humboldt Universität zu Berlin

We calculate 2D frequency resolved spectra for the FMO complex non-perturbatively in the field. This is possible due to the summation of the polarizations for a number of randomly placed complexes, each one excited with a phase related to its position. Since orientational averaging and energetic disorder can be included at the same time the additional computational effort is moderate. The low intensity spectra are compared with the experimental ones [1] and show good agreement.

The advantage of the presented method is that the intensity dependence of the 2D spectrum can be investigated, as well as the signal from higher order phase matched directions. Furthermore the inclusion of shaped laser pulses is easily possible.

[1] T. Brixner et al., Nature 434, 625 (2005).

MO 64.6 Fr 15:15 6F

Optimal Control of Multi-Photon Ionization of Rubidium Molecules in a MOT — •F. Weise[1], S. Birkner[1], A. Merli[1], S. M. Weber[1], F. Sauer[1], L. Wöste[1], A. Lindinger[1], W. Salzmann[2], T. G. Mullins[2], J. Eng[2], M. Albert[2], R. Wester[2], and M. Weidemüller[2] — [1]Freie Universität Berlin — [2]Universität Freiburg

In the recent years the processes in ultra-cold atomic ensembles have been extensively studied and many fascinating effects have been discovered. Expanding these investigations to molecules is a further logical step to gain knowledge about fundamental quantum dynamics and is a highly discussed topic in theory [1].

We apply optimal control techniques and shaped femtosecond laser pulses to investigate ultra-cold molecules in a magneto-optical trap [2]. In the presented experiment the multi-photon ionization of rubidium dimers is optimized and the resulting optimal pulse exhibits two frequency bands in the spectrum. Further investigation of those bands provides information about the ionization process and the involved electronic states.

This successful implementation of coherent control on ultra-cold molecules opens the pathway to new prospects.

[1] C.P. Koch, R. Kosloff and F. Masnou-Seeuws, Phys. Rev. A, 73,043409, 2006.

[2] W. Salzmann et. al., Phys. Rev. A, 73, 023414, 2006.

MO 64.7 Fr 15:30 6F

Molecular quantum computing with vibrational qubits in $MnBr(CO)_5$ — Brigitte Schneider[1], •Ulrike Troppmann[2], Karl Kompa[1], and Regina de Vivie-Riedle[2] — [1]MPI für Quantenoptik, Hans-Kopfermann-Str. 1, 85748 Garching — [2]LMU Department Chemie, Butenandt-Str. 11, 81377 München

We use Manganese-pentacarbonyl-bromide [$MnBr(CO)_5$] as a processor unit for quantum computing[2]. The qubits encoded in two strong IR-active vibrational normal modes are operated by laser pulses in the femto- to picosecond range. Different logical operations are achieved by special pulse shapes optimized via Optimal Control Theory (OCT). For the universal sets of elementary global quantum gates simply structured pulses with low energies about 1 μJ and high switching efficiencies above 99% are obtained. With regard to experimental realization the molecule is immobilized in a siliconoxide structure (MFI zeolite). Environmental interactions and other side effects influencing the controllability of the molecule are discussed.

[1]B. M. R. Korff, U. Troppmann, K. L. Kompa and R. de Vivie-Riedle, JCP 123 (2005) 244509

MO 64.8 Fr 15:45 6F

A compact molecular interferometer for surface science and nanotechnology — •András Major and Markus Arndt — Fakultät für Physik, Universität Wien, Boltzmanngasse 5, A-1090 Wien

We present the first results obtained from our new Talbot-Lau interferometer that uses the screen method for detection. This work discusses the new possibilities of the novel set-up and also outlines potential applications such as nanopatterning and quantum information.

MO 65: Ultracold Molecules II (gemeinsam mit Q)

Zeit: Freitag 14:00–15:45 Raum: 6J

Gruppenbericht MO 65.1 Fr 14:00 6J

A Mott-like State of Molecules — •Stephan Dürr, Thomas Volz, Niels Syassen, Dominik Bauer, Eberhard Hansis, and Gerhard Rempe — Max-Planck-Institut für Quantenoptik, Hans-Kopfermann-Straße 1, 85748 Garching, Germany

Mott insulators of ultracold gases in optical lattices bear a great potential for applications in quantum simulations and quantum information processing, in particular when using particles with a long-range dipole-dipole interaction, such as polar molecules. Here we show the realization of a Mott-like state of molecules. The molecules are produced from an atomic Mott insulator with a density profile chosen such that the central region of the gas contains two atoms per lattice site. A Feshbach resonance is used to associate the atom pairs to molecules. Remaining atoms can be removed with blast light. In order to show that the resulting state has exactly one molecule per lattice site, the molecules are dissociated and the lattice depth is reduced. This restores phase coherence which is seen in time-of-flight images. Additional information is obtained from measurements of the excitation spectrum [1].

[1] T. Volz et al. *Nature Physics* **2**, 692–695 (2006).

MO 65.2 Fr 14:30 6J

Resonant enhancement in ultracold atom-dimer scattering — •Steven Knoop[1], Michael Mark[1], Francesca Ferlaino[1], Johann Georg Danzl[1], Harald Schöbel[1], Tobias Kraemer[1], Hanns-Christoph Nägerl[1], and Rudi Grimm[1,2] — [1]Institut für Experimentalphysik, Universität Innsbruck, Austria — [2]Institut für Quantenoptik und Quanteninformation, Innsbruck, Austria

Ultracold quantum gases with tunable interaction yield the unique possibility to study universal properties of resonantly interacting few-body systems. A clear example has been the experimental evidence for Efimov quantum states in an ultracold Cs gas [1]. Their signature was found in a giant three-body loss feature due to resonant coupling between three free atoms and an Efimov trimer. Following the Efimov scenario an Efimov trimer can also couple to an atom and a dimer [2].

Here we will report on the experimental observation of resonant enhancement in the inelastic atom-dimer collision rate. By means of Feshbach association ultracold dimers in a weakly bound s-wave state are produced and trapped in an optical dipole trap [3]. Together with the remaining atoms they form an atom-dimer mixture which is at a temperature of 250 nK. By selectively measuring the loss of dimers the inelastic atom-dimer collision rate is obtained. A resonance in the collision rate at a scattering length of 400 Bohr radii is found which might represent an atom-dimer Efimov resonance.

[1] T. Kraemer et al, Nature 440, 315 (2006); [2] E. Braaten and H.-W. Hammer, Phys. Rep. 428, 259 (2006); [3] M. Mark et al, submitted to PRA (2007)

MO 65.3 Fr 14:45 6J

Formation and Detection of ultracold LiCs molecules — •Jörg Lange, Stephan Kraft, Johannes Deiglmayr, Christian Giese, Leif Vogel, Christian Glück, Peter Staanum, Roland Wester, and Matthias Weidemüller — Physikalisches Institut, Universität Freiburg, 79104 Freiburg, Germany

We report on the first observation of ultracold LiCs molecules, formed by the trapping light in a double species magneto optical trap. After one-colour two-photon ionization, the molecules are detected with high resolution time-of-flight mass spectrometry. The molecule formation rate coefficient is found to be in the range of $10^{-18}\,\mathrm{cm^3\,s^{-1}}$ to $10^{-16}\,\mathrm{cm^3\,s^{-1}}$ [1]. This is an order of magnitude smaller than for other heteronuclear alkali dimers formed under comparable condtions, but in agreement with predictions.

In current experiments, we study controlled photoassociation via the $[\mathrm{Li}(2S_{3/2})+\mathrm{Cs}(6P_{3/2})]$-asymptote to increase the production rate of electronic ground state molecules. Together with a more detailed investigation of the resonantly enhanced two-photon ionization process, precise information on the rovibrational structure of the involved LiCs-potentials can be obtained.

[1] S. D. Kraft *et al.*, J. Phys. B **39**, S 993 (2006)

MO 65.4 Fr 15:00 6J

Experiments with an ultracold ^{6}Li-^{40}K Fermi-Fermi mixture — •Eric Wille[1,2], Frederik Spiegelhalder[1], Gabriel Kerner[1], Devang Naik[1], Andreas Trenkwalder[1,2], Clarice Aiello[1,2], Raquel Chulia-Jordan[1], Gerhard Hendl[1], Florian Schreck[1], and Rudolf Grimm[1,2] — [1]Institut für Quantenoptik und Quanteninformation, Österreichische Akademie der Wissenschaften, Innsbruck, Austria — [2]Institut für Experimentalphysik, Innsbruck, Austria

Degenerate mixtures of the two fermionic species ^{6}Li and ^{40}K provide a new, intriguing many-body quantum system, which allows to study strongly interacting Fermi gases consisting of atoms with unequal masses. We have recently created our first molecular $^6Li_2$ BEC in a newly build machine. The ^{6}Li atoms were loaded into a crossed-beam optical dipole trap realized with a 100 W near-infrared fiber laser. The sample was cooled evaporatively by lowering the laser power by three orders of magnitude within 5 s, leading to quantum degeneracy of $^6Li_2$. To study heteronuclear mixtures, we have simultaneously trapped ^{40}K and ^{6}Li. We have sympathetically cooled ^{40}K with ^{6}Li during the evaporation process in the dipole trap. We will present our first investigations on heteronuclear interactions.

MO 65.5 Fr 15:15 6J

Molecular wavepacket oscillations of ultracold Rb_2 — •A. Merli[1], S. Weber[1], F. Sauer[1], M. Plewicki[1], F. Weise[1], S. Birkner[1], L. Wöste[1], A. Lindinger[1], W. Salzmann[2], J. Eng[2], T.G. Mullins[2], M. Albert[2], R. Wester[2], and M. Weidemüller[2] — [1]Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, D 14195 Berlin — [2]Physikalisches Institut, Universität Freiburg, Hermann Herder Str. 3, D 79104 Freiburg i. Br.

Our long-term aim is the efficient formation and vibrational cooling of ultracold Rb_2 molecules to their vibrational ground state by pump-dump like processes via an intermediate excited state, theoretical predicted by [1]. First pump-probe experiments with femtosecond light pulses in a dark SPOT magneto-optical trap were successfully performed in order to gain information about the molecular dynamic in the excited state of the Rb-Dimer. The observed wavepacket oscillation periods are depending from the cut-off of the spectral frequencies (made in the Fourier plane of a zero-dispersion compressor) in the pump pulse below the Rb atomic D1 and D2 resonances, respectively. Linear chirps of the excitation pulse influence the pump-probe spectra. Measurements at different bright state fractions [2] of the trapped molecules provide advice about the origin of the molecules which are oscillating.

[1] C. P. Koch, R. Kosloff, and F. Masnou-Seeuws, Phys. Rev . A, 73, 043409, 2006

[2] C.G. Townsend, N.H. Edwards, K.P. Zetie, C.J.Cooper, J. Rink, and C.J Foot, Phys. Rev.A 53, 1702, 1996

MO 65.6 Fr 15:30 6J

Temperature shift of a triatomic Efimov resonance in an ultracold gas of cesium atoms — •Almar Lange[1], Bastian Engeser[1], Karl Pilch[1], Andrea Prantner[1], Hans-Christoph Nägerl[1], and Rudolf Grimm[1,2] — [1]Institut für Experimentalphysik, Innsbruck, Austria — [2]Institut für Quantenoptik und Quanteninformation, Österreichische Akademie der Wissenschaften

We report on measurements of three-body recombination at negative scattering lengths in an ultracold cesium gas. Magnetic tuning of the scattering length by means of a Feshbach resonance is used to investigate a strong loss peak resulting from an Efimov resonance. The position of maximum loss shifts significantly when the temperature of the gas is varied, providing quantitative insight into the evolution of an Efimov state into a triatomic continuum resonance. We compare our measurements with several calculations that extend the theory of three-body recombination to non-zero collision energies.

In our apparatus we prepare an ultracold gas of cesium atoms in an optical surface trap. The main part is a glass cell with an integrated prism, providing good optical access and accurate and fast control of the magnetic field. The atoms are located a few micrometers above the dielectric prism surface. Raman sideband and Sisyphus cooling are applied to reach temperatures of a few μK. We further reduce the temperature below 100nK via evaporative cooling. We then apply different magnetic fields and measure the rate of three-body recombination.