

## MO 13: Molekülphysik Poster 1

Zeit: Dienstag 16:30–19:00

Raum: VMP 8 Foyer

MO 13.1 Di 16:30 VMP 8 Foyer

**The impact of geometry on the fluorescence kinetics of poly(perylene bisimide acrylate)** — ●FLORIAN SPREITLER<sup>1</sup>, MICHAEL SOMMER<sup>2</sup>, MUKUNDAN THELAKKAT<sup>2</sup>, and JÜRGEN KÖHLER<sup>1</sup> — <sup>1</sup>Experimentalphysik IV and BIMF, Universität Bayreuth, Universitätsstrasse 30, 95447 Bayreuth, Germany — <sup>2</sup>Angewandte Funktionsspolymere, Makromolekulare Chemie I, Universität Bayreuth, Universitätsstrasse 30, 95447 Bayreuth, Germany

Poly(perylene bisimide acrylate) is a novel electron conducting polymer with potential applications in organic photovoltaics and organic field effect transistors. Its steady-state absorption and fluorescence spectra feature considerable differences with respect to the monomer spectra. These are attributed to the aggregation of the perylene bisimide pendant groups.

Here we report on time-resolved ensemble fluorescence experiments on solutions of poly(perylene bisimide acrylate) as a function of chain length. We used a streak-camera setup to monitor spectrally resolved fluorescence decays on timescales between 1 ps and 100 ns. An insight into the geometry of the polymer is obtained by comparing our results with the predictions of the Frenkel exciton theory for different arrangements of the chromophore groups.

MO 13.2 Di 16:30 VMP 8 Foyer

**Fourier-transform spectroscopy on Sr<sub>2</sub> for modeling cold collisions** — ●ALEXANDER STEIN, HORST KNÖCKEL, and EBERHARD TIE-MANN — Leibniz Universität Hannover, Welfengarten 1, 30167 Hannover

Strontium could be a candidate for a new optical frequency standard (see e.g. A. D. LUDLOW et al., *Science* **319**, 1805 (2008)). Hence there is high interest in cooling and trapping of cold strontium atoms. Additionally, ultracold Sr<sub>2</sub> molecules are proposed to offer good opportunities for new and exciting experiments as the precise measurement of the time variation of the electron-proton mass ratio (T. ZELEVINSKY, S. KOTOCHIGOVA, AND J. YE, *Phys. Rev. Lett.* **100**, 043201 (2008)). Nevertheless there are no sufficiently precise ground state potentials available for the Sr<sub>2</sub> molecule allowing the direct calculation of collisional properties like the scattering length, and still only few of the excited electronic states are spectroscopically investigated.

We report on new spectroscopic investigations by Fourier-transform spectroscopy of laser induced fluorescence in a heat pipe setup. Our derived potentials show significant deviations compared to the previously most precise work (G. GERBER, R. MÖLLER, AND H. SCHNEIDER, *J. Chem. Phys.* **81**, 1538 (1984)) due to a change in the rotational assignment.

The current status of the experiment and improved potentials of the  $X^1\Sigma_g^+$  ground state (including the long range region) and excited state  $2(A)^1\Sigma_u^+$  will be presented. Improved estimations of the ground state scattering lengths for all combinations of natural isotopes are given.

MO 13.3 Di 16:30 VMP 8 Foyer

**Fluorescence and lifetime of the [Ni<sub>3</sub>(4-methoxyphenylpyrazole)<sub>6</sub>] complex** — ●YVONNE SCHMITT<sup>1</sup>, SUSANN BERGNER<sup>2</sup>, WERNER THIEL<sup>2</sup>, and MARKUS GERHARDS<sup>1</sup> — <sup>1</sup>Physikalische und Theoretische Chemie, TU Kaiserslautern, Erwin Schrödinger-Str. 52, 67663 Kaiserslautern — <sup>2</sup>Anorganische Chemie, TU Kaiserslautern

With respect to catalytic and magnetic properties the investigation of complexes containing more than one metal atom is of great interest. Here we investigate a complex containing three Ni atoms: [Ni<sub>3</sub>(4-methoxyphenylpyrazole)<sub>6</sub>], by applying fluorescence spectroscopy which has a high sensitivity with respect to changes in structure and environment. The measurements are performed in an acetonitrile and dichlormethane solution as a function of the excitation energy. For specific electronic transitions the lifetime is determined by analyzing the phase shift and modulation of the fluorescence light, i.e. lifetimes down to about 10 ps can be determined by frequency domain measurements. Another interesting point is the feasible reaction of the complex with oxygen. Furthermore the concentration dependence with respect to the formation of aggregates is discussed.

MO 13.4 Di 16:30 VMP 8 Foyer

**Single-molecule spectroscopy of perylene bisimide multichromophoric assemblies at cryogenic temperatures** —

●ABEY ISSAC<sup>1</sup>, CATHARINA HIPPIUS<sup>2</sup>, FRANK WÜRTHNER<sup>2</sup>, and JÜRGEN KÖHLER<sup>1</sup> — <sup>1</sup>Experimentalphysik IV, Universität Bayreuth, 95440 Bayreuth, Germany — <sup>2</sup>Institut für Organische Chemie and Röntgen Research Center for Complex Material Systems, Universität Würzburg, 97074 Würzburg, Germany

We present the characterization of the photophysical parameters of multichromophoric dye assemblies based on perylene bisimide dyes as a function of their geometry. In order to avoid ensemble averaging and thermal line broadening effects, we employed low-temperature single-molecule spectroscopy.

MO 13.5 Di 16:30 VMP 8 Foyer

**Energy- and charge-transfer processes in flexible organic donor-acceptor dyads** — ●CHRISTIANE HOFMANN<sup>1</sup>, PETER BAUER<sup>2</sup>, SAIF HAQUE<sup>3</sup>, MUKUNDAN THELAKKAT<sup>2</sup>, and JÜRGEN KÖHLER<sup>1</sup> — <sup>1</sup>Experimentalphysik IV und BIMF, Universität Bayreuth, D-95440 Bayreuth, Deutschland — <sup>2</sup>Applied Functional Polymers, Universität Bayreuth, D-95440 Bayreuth, Deutschland — <sup>3</sup>Department of Chemistry, Imperial College London, London SW7 2AZ, UK

We investigated energy- and electron-transfer processes in organic donor-acceptor dyads with complementary spectroscopic techniques. In these dyads, a triphenylamine (TPD) donor was linked to a perylenebisimide (PBI) acceptor by a flexible, non-conjugated bridge. Time-resolved fluorescence spectroscopy revealed a quenching of the donor emission, accompanied by a corresponding rise of the acceptor fluorescence. Additionally, we found a second quenching process affecting the acceptor fluorescence. The length as well as the chemical structure of the bridge between the donor and acceptor moieties were found to have a strong impact on the rates of both quenching processes while changing the solvent influenced mainly the rate of acceptor quenching. The possibility of an electron-transfer process from PBI to TPD being responsible for the additional acceptor quenching has been studied by transient absorption spectroscopy.

MO 13.6 Di 16:30 VMP 8 Foyer

**Substituted dipolar phenothiazines for efficient dye-sensitized solar cells** — ●MATTHIAS STOLTE<sup>1</sup>, THOMAS MÜLLER<sup>2</sup>, MARTINA HAUCK<sup>2</sup>, and HANS-GEORG KUBALL<sup>1</sup> — <sup>1</sup>Department of Chemistry, Technische Universität Kaiserslautern, 67663 Kaiserslautern, Germany — <sup>2</sup>Department of Macromolecular and Organic Chemistry, Heinrich-Heine Universität Düsseldorf, 40225 Düsseldorf, Germany

Since Grätzel [1] et al. reported about high solar energy-to-electricity conversion for dye-sensitized solar cells much effort was spent on the synthesis of organic chromophores. The electron rich heterocycle phenothiazine exhibit an intensive charge transfer upon excitation with UV/VIS light. Tuning of the optical and electrochemical properties by different strong donor and acceptor groups and variation of the substitution pattern give excess to a huge variety of promising candidates for dye-sensitized solar cells. In this work we present the physico-chemical characterization, including cyclic voltammetry, electro-optical absorption and emission spectroscopy of two series of push-pull chromophores containing phenothiazine as a donor group. Especially changes of polarity can be probed by measurement of the electrochromism of the chromophores in solution. A new highly sensitive and also automated spectrometer for electrooptical absorption spectroscopy was developed in our group in order to obtain properties of the ground and the lowest excited state. The influence of different polar substituents on the chromophore will be discussed on the basis of experimental data as well as DFT calculations.

[1] B. O Regan, M. Grätzel, *Nature* 1991, 353, 737.

MO 13.7 Di 16:30 VMP 8 Foyer

**Competing ultrafast photo-induced ring closure and E-Z isomerization of a photochromic furylfulgide** — ●RON SIEWERTSEN, FALK RENTH, and FRIEDRICH TEMPS — Institut für Physikalische Chemie, Christian-Albrechts-Universität zu Kiel, Olshausenstr. 40, D-24098 Kiel

Fulgides and their derivatives are thermally irreversible photochromic switches with high application potential. Their photochromism is based on the photo-reversible interconversion between the open (*E*)- and the closed (*C*)-isomer. The photo-induced *E*→*C* ring closure and the competing *E*→*Z* isomerization reactions of the (*E*)-

isomer of the furylfulgide 1-[1-(2,5-dimethyl-3-furyl)-ethylidene]-2-isopropylidene succinic anhydride in *n*-hexane have been studied using femtosecond time-resolved spectroscopy. Transient absorption measurements after excitation at  $\lambda = 335$  nm provide clear evidence for an ultrafast branching into the two reaction channels within 250 fs with a (*C*) : (*Z*) product ratio of about 2 : 1. Two observed time constants for the product formation of (*C*) and (*Z*) (0.10 and 0.25 ps) suggest that both reactions proceed *via* distinct conical intersections. Oscillations of the transient absorption with frequencies of 64 and 114  $\text{cm}^{-1}$  are interpreted as excited-state vibrations during the *E*→*Z* isomerization reaction. Time-dependent DFT geometry optimizations were performed to gain insight into the involved reaction coordinates. Our results are of interest for the understanding of competing ultrafast reactions in polyatomic molecules and the ability to influence the branching by coherent control techniques.

MO 13.8 Di 16:30 VMP 8 Foyer

**Photoisomerization of  $\text{C}_5\text{H}_4\text{NH}$ : Molecular symmetry, non-adiabatic couplings and quantum dynamics** — MICHAEL BAER<sup>1</sup>, OMAR DEEB<sup>2</sup>, SALIH JABOUR<sup>2</sup>, •MONIKA LEIBSCHER<sup>3</sup>, JÖRN MANZ<sup>3</sup>, and SHMUEL ZILBERG<sup>4</sup> — <sup>1</sup>Fritz Haber Institut für Molecular Dynamics, The Hebrew University of Jerusalem, Israel — <sup>2</sup>Faculty of Pharmacy, Al-Quds University, Palestine — <sup>3</sup>Institut für Chemie und Biochemie, Freie Universität Berlin, Germany — <sup>4</sup>Department of Physical Chemistry and Farkas Center for Light Induced Processes, The Hebrew University of Jerusalem, Israel

An important step towards the design of laser pulses for the control of torsional switches is the evaluation of the relevant non-adiabatic coupling terms (NACTs) which may induce the transition from the photo-excited reactant to the product. Prominent effects are expected near conical intersections. We derive the symmetry properties of the conical intersections and NACTs according to the molecular symmetry group which may serve to test quantum chemistry calculations of the NACTs. Those symmetry results are demonstrated for the model system  $\text{C}_5\text{H}_4\text{NH}$  which has the molecular symmetry  $C_{2v}(M)$ . Moreover, we show that the NACTs of  $\text{C}_5\text{H}_4\text{NH}$  obey quantization rules. We present the results of quantum dynamical simulations of laser induced molecular torsion on the three coupled electronic states and show how the torsional dynamics depends on the strength and symmetry of the NACTs.

Financial support by the Deutsche Forschungsgemeinschaft (project Ma 515/22-2) is gratefully acknowledged.

MO 13.9 Di 16:30 VMP 8 Foyer

**Probing the geometry dependence of molecular dimers with 2D-vibronic spectroscopy** — •JOACHIM SEIBT, KLAUS RENZIEHAUSEN, DIMITRI V. VORONINE, and VOLKER ENGEL — Institut für Physikalische Chemie, Am Hubland, 97074 Würzburg

Two-dimensional vibronic correlation spectra of molecular dimers are calculated, taking a single vibration in each monomer into account. Within the employed wave function approach, the coupling to a surrounding is included only phenomenologically. It is shown that this offers a straightforward understanding of the spectra. The influence of the relative orientation of the monomer transition dipole-moments and the electronic coupling strength is investigated. Employing a model for perylene bisimide we predict the 2D-spectra for the monomer and dimer configurations.

MO 13.10 Di 16:30 VMP 8 Foyer

**The Role of Vibrational Hot States on Pump-DFWM and CARS Experiments** — •MAHESH NAMBOODIRI, JÖRG LIEBERS, VINU NAMBOODIRI, ABRAHAM SCARIA, GÜNTER FLACHENECKER, ULRICH KLEINEKATHÖFER, and ARNULF MATERNY — Jacobs University Bremen, Germany

The dynamics of electronic excited states of the bromine molecular system can be investigated in detail using pump-DFWM (degenerate four-wave mixing) and CARS (coherent anti-Stokes Raman scattering) techniques. The pump-DFWM experiments revealed that, by varying the DFWM wavelength, two clearly separated vibrational wave packets with oscillation periods of 395 and 510 fs could be observed, which correspond to a clear spacing of excited vibrational modes in the B state. This is due to contributions from vibrational hot states in the electronic ground state (X). Quantum dynamical calculations showed that for a pump wavelength of 540 nm, the Franck-Condon overlap from the first vibrational hot state for the  $B \leftarrow X$  transition is considerably better than that found for transitions from the vibrational ground state of the X state. CARS experiments were performed in or-

der to substantiate these findings. Here, the pump wavelength was kept fixed at 540 nm while both the Stokes wavelength and the temperature were varied. At higher temperatures an increase of hot state contributions to the observed B state dynamics was found. The detuning of the Stokes wavelength selectively probed the hot state contributions even at room temperature. The experimental and theoretical results were in good agreement with previous observations.

MO 13.11 Di 16:30 VMP 8 Foyer

**Quantum dynamical simulations of femtosecond pump-DFWM spectroscopy of higher excited states** — •JÖRG LIEBERS, ABRAHAM SCARIA, ARNULF MATERNY, and ULRICH KLEINEKATHÖFER — Jacobs University Bremen, Germany

Time- and frequency-resolved four-wave mixing (FWM) spectroscopy is a major tool to investigate dynamical properties of molecules. Until now the dynamics of the ground state and lower lying excited states of small molecules were well investigated in numerous experiments. By using a combination of an initial pump pulse and a degenerate four-wave mixing (DFWM) process, we show that the vibrational dynamics occurring in high-lying electronic states of molecules can be monitored as well. Experiments and simulations were performed on molecular bromine, where specific Franck-Condon overlaps between the  $B(^3\Pi_u^+)$  and an ion pair state can be used to probe different parts of the excited state dynamics individually and therefore indirectly the contributions from different vibrational states in the electronic ground state. It is possible to selectively probe contributions of the hot vibrational states at room temperature. Here we present the results of quantum dynamical simulations which explain the details of this complex scenario. The experiments are detailed in a separate contribution.

[1] A. Scaria, V. Namboodiri, J. Konradi, A. Materny, Phys. Chem. Chem. Phys. **10** (2008) 983.

MO 13.12 Di 16:30 VMP 8 Foyer

**Fragmentation of CO Molecules in Ultra-short, CEP stabilized Laser Pulses** — •MANUEL KREMER<sup>1</sup>, ARTEM RUDENKO<sup>2</sup>, BETTINA FISCHER<sup>1</sup>, RAM GOPAL<sup>1</sup>, KONSTANTIN SIMEONIDIS<sup>1</sup>, KAI-UWE KÜHNEL<sup>1</sup>, OLIVER HERRWERTH<sup>3</sup>, ADRIAN WIRTH<sup>3</sup>, SERGEY ZHEREBTSOV<sup>3</sup>, MATTHIAS LEZIUS<sup>3</sup>, MATTHIAS KLING<sup>3</sup>, FERENC KRAUSZ<sup>3</sup>, CLAUS DIETER SCHRÖTER<sup>1</sup>, ROBERT MOSHAMMER<sup>1</sup>, and JOACHIM ULLRICH<sup>1</sup> — <sup>1</sup>Max-Planck-Institut für Kernphysik, Saupfercheckweg 1, 69117 Heidelberg, Germany — <sup>2</sup>Max-Planck Advanced Study Group within CFEL, Notkestrasse 85, 22607 Hamburg, Germany — <sup>3</sup>Max-Planck-Institut für Quantenoptik, Hans Kopfermannstr. 1, 85748 Garching, Germany

We present fully differential data on single and double ionization of CO molecules in ultra short (4fs), linearly polarized, intense (up to  $1\text{PW}/\text{cm}^2$ ) laser pulses measured with a \*Reaction Microscope\*.

Depending on the carrier-envelope-phase (CEP) of the laser pulses we see strong changes in the momentum distributions and emission directions of created  $C^+$  and  $C^{++}$  ions. This is a clear indication for geometrical alignment of the molecule in the ultra short pulse.

The CEP-dependent asymmetry parameters ( $A = \frac{N_L - N_R}{N_L + N_R}$ , where  $N_L$  and  $N_R$  means the number of fragments emitted to the left and to the right hemisphere, respectively) for dissociation ( $CO \rightarrow C^+ + O$ ) and Coulomb explosion ( $CO \rightarrow C^+ + O^+$ ) exhibit a phase shift of about  $\pi/2$  with respect to each other. Experimental results and first interpretations will be presented.

MO 13.13 Di 16:30 VMP 8 Foyer

**Surface-enhanced femtosecond CARS spectroscopy** — •VINU NAMBOODIRI, GABRIEL CAVA DIAZ, MAHESH NAMBOODIRI, GÜNTER FLACHENECKER, and ARNULF MATERNY — Jacobs University Bremen, Bremen, Germany

Surface-enhanced Raman scattering (SERS) has become an integral part of spectroscopy. The inelastic scattering process is enhanced by several orders of magnitude when molecules are in close contact to nano structured coin metals. However, the use of surface enhancement in combination with nonlinear spectroscopy is by far not as common as in linear spectroscopy even though a more drastic effect could be expected. In our work, we investigate the surface enhancement mechanisms in combination with coherent anti-Stokes Raman scattering (CARS) using femtosecond laser pulses. Silver (and gold) colloids were used as enhancement medium. Molecules, which show conventional SERS were selected for the experiments. Femtosecond-CARS was performed on these molecular systems in the presence and absence of silver colloids. The scattered CARS signal was collected at different angles with respect to the incoming beams and the results were compared

to gain information about the enhancement effects on the vibrational dynamics of the molecular system.

Earlier results: E.J. Liang, A. Weippert, J.-M. Funk, A. Materny, W. Kiefer, Chem. Pys. Lett. 227, 115 (1994)

MO 13.14 Di 16:30 VMP 8 Foyer

**Pump-probe experiments on  $CO_2$  in ultra-short intense laser pulses** — ●BETTINA FISCHER<sup>1</sup>, MARKUS SCHÜRHOLOZ<sup>1</sup>, MANUEL KREMER<sup>1</sup>, ARTEM RUDENKO<sup>2</sup>, SERGUI PATCHKOVSKI<sup>3</sup>, OLGA SMIRNOVA<sup>3</sup>, CLAUS DIETER SCHRÖTER<sup>1</sup>, ROBERT MOSHAMMER<sup>1</sup>, and JOACHIM ULLRICH<sup>1</sup> — <sup>1</sup>Max-Planck-Institut für Kernphysik, Saupfercheckweg 1, 69117 Heidelberg, Germany — <sup>2</sup>Max-Planck Advanced Study Group within CFEL, Notkestrasse 85, 22607 Hamburg, Germany — <sup>3</sup>National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada

The fragmentation dynamics of  $CO_2$  in linearly polarized, intense ( $10^{14}W/cm^2$ ) and ultra-short (7fs) laser pulses was studied in pump-probe experiments. Using a Reaction Microscope all created heavy fragments have been detected in coincidence.

A modulation of the  $CO_2^+$  count rate as function of the delay time between pump and probe pulse was observed. It is caused by coherent superposition of several vibrational states of  $CO_2^+$  which are created in the first pump pulse. Their time-dependent ionization probability is then probed by the second pulse. Three modulation frequencies can be identified and are compared to spectroscopic data. Theoretical results for the excitation probabilities of the vibrational  $CO_2^+$  states are in good agreement with the present results and allow the identification of the contributing molecular states.

MO 13.15 Di 16:30 VMP 8 Foyer

**Excited-state dynamics of cytosine tautomers** — ●KYRIAKI KOSMA, CHRISTIAN SCHROETER, THOMAS SCHULTZ, and INGOLF V. HERTEL — Max-Born-Institut fuer Nichtlineare Optik und Kurzzeit-spektroskopie, Max-Born-Str. 2A, D-12489 Berlin-Adlershof, Germany

The relaxation dynamics of DNA bases have been extensively studied in the 200-300 nm spectral region [1].

For cytosine, the most stable tautomers in the gas phase are the enol, keto, and keto-imino forms [2], each one absorbing in different regions in the UV [3]. Existing pump-probe experiments study the excited-state lifetime of the enol tautomer with an excitation wavelength of 267 nm [4], while most theoretical studies concentrate on the keto tautomer, the second most stable form [5, 6].

We disentangled the different relaxation dynamics of the cytosine tautomers, by exciting the molecules in a cold molecular beam with five different wavelengths in the range 260-290 nm. Different lifetimes were observed and assigned to two of the tautomers, i.e. the enol and keto forms. A long lifetime of >200 ps was observed for the first time and assignment to the triplet state of keto-cytosine is proposed.

- [1] Carlos E. et al., Chem. Rev. 2004, 104, 1977
- [2] Tomic K. et al., J. Phys. Chem. A 2005, 109, 8410
- [3] Nir E. et al., Chem. Phys. Lett. 2002, 355, 59
- [4] Kang H. et al., J. Am. Chem. Soc. 2002, 124, 12958
- [5] Ismail N. et al., J. Am. Chem. Soc. 2002, 124, 6818
- [6] Zgierski M. Z. et al., Chem. Phys. Lett. 2008, 463, 289

MO 13.16 Di 16:30 VMP 8 Foyer

**Time-resolved photoelectron spectroscopy from liquid samples** — ●ANDREA LÜBCKE, THOMAS SCHULTZ, and INGOLF VOLKER HERTEL — Max-Born-Institut für Nichtlineare Optik und Kurzzeit-spektroskopie, Max-Born-Strasse 2A, 12489 Berlin

Photoelectron spectroscopy is a powerful tool to study electronic ground and excited states in gas phase as well as solid states. Photoelectron spectroscopy from liquids became possible by exploiting liquid jets and were first performed at synchrotron light sources. Here, we combine the liquid jet technique with a short pulse laser system to perform fs time-resolved electron spectroscopy to study photochemical processes in liquids. The experimental setup is described and first experimental results are discussed.

MO 13.17 Di 16:30 VMP 8 Foyer

**Dynamics of elementary excitations in para-hydrogen crystals: long living, coherent phonons, rotors and stimulated rotational Raman beats** — ●FALK KÖNIGSMANN, NINA OWSCHIMIKOW, and NIKOLAUS SCHWENTNER — Freie Universität Berlin, Institut für Experimentalphysik, Arnimallee 14, D-14195 Berlin

One of the most distinct spectroscopic features of cryogenic para-

hydrogen are the sharp linewidths. The thus expected very long coherence times in the dynamics did however not show up in previous ultrashort pulsed excitations. Our approach is ultrashort, spectrally resolved Optical Kerr Effect (OKE) spectroscopy, sensitive to induced anisotropies. We grow 3 cm long, transparent para-hydrogen crystals in an enclosed cell at 10 K, which are then cooled down to 4 K. The crystals are pumped with 150 fs pulses at 780 nm of a Ti:Sa amplified laser system and the induced birefringence is detected with the second harmonic in a colinear way. We observe a long lasting (>20 ps) sinusoidal birefringence modulation with a period of 907 fs. It coincides with the transverse, optical phonon at the center of the Brillouin-zone, which is observed exclusively in Raman scattering. We also observed long lasting (>80 ps), higher frequency birefringence modulations with a period of 94 fs and pump-induced, stimulated Stokes- and Anti-Stokes Raman bands of the detected second harmonic. Both match the J=2 rotor excitation of 355 wavenumbers. The latter carries a 17 ps beating structure, which corresponds to the 2.0 wavenumbers splitting in the rotor triplet also known from cw Raman-spectroscopy.

MO 13.18 Di 16:30 VMP 8 Foyer

**Rotational dephasing and depopulation rates measured via non-adiabatic alignment** — ●NINA OWSCHIMIKOW<sup>1</sup>, JOCHEN MAURER<sup>1</sup>, FALK KÖNIGSMANN<sup>1</sup>, BURKHARD SCHMIDT<sup>2</sup>, and NIKOLAUS SCHWENTNER<sup>1</sup> — <sup>1</sup>Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin — <sup>2</sup>Institut für Mathematik, Freie Universität Berlin, Arnimallee 6, 14195 Berlin

Under ambient conditions, bimolecular collisions in gases, and therefore decoherence and dissipation, occur on a picosecond time scale. The dynamics of non-adiabatic laser induced alignment in nitrogen covers exactly this time range and is extremely well described by theory, which allows to quantitatively study relaxation processes of both phase and population. In the experiment, the excitation is followed by recurrent transient bursts of molecular alignment reflecting the phase coherence, which are monitored in a homodyne detected optical Kerr effect experiment. Additionally a non-equilibrium population of M quantum numbers is created upon excitation and is reflected in a weak structureless offset in the detected signal, which is nevertheless amplified by the coherent oscillations due to the quadratic detection. By decomposing the theoretically calculated signal into a coherence part and a population part [1] with two different decay rates and fitting to our data, we show that a slower thermalization of population compared to phase relaxation results in a change of revival shape over time, and thus both rates can be extracted directly from an alignment experiment.

[1] S. Ramakrishna and T. Seideman, Phys. Rev. Lett. 95, 113001 (2006)

MO 13.19 Di 16:30 VMP 8 Foyer

**Trapping and cooling of single molecular ions for time resolved vibrational spectroscopy** — ●GÜNTHER LESCHHORN, STEFFEN KAHRA, HSIANG-TAI DOU, WOLFRAM SCHMID, WERNER FUSS, and TOBIAS SCHAETZ — Max-Planck-Institut für Quantenoptik, Garching

We report the preparation of externally cold and well localized molecular ions (spacial resolution of a micrometer). By exploiting numerous techniques like ion-trapping, sympathetic laser cooling and light pressure separation we are able to provide and trap a selectable amount of molecular ions (from a few hundred down to a single one). The trapped molecular ions can serve as targets for time resolved diffraction experiments with a resolution of a few fs and below to observe fast structural changes. As a first step towards this goal we propose vibrational spectroscopy on a single magnesium hydride ion ( $MgH^+$ ), using a UV-pump UV-probe (300 nJ, pulse duration below 4 fs) scheme. A coherent oscillating wave packet of an excited bound state with a period of 30.9 fs is mapped on a dissociative channel. The intramolecular distance at a given time delay between pump and probe pulse defines the required wavelength to dissociate the  $MgH^+$ . If this wavelength lies within the spectrum of the UV-probe pulse, the molecular ion dissociates with higher probability compared to the case when the wavelength lies significantly outside the spectrum. The oscillation period of the wave packet can thus be measured by observing the variation of the loss rate (dissociation) of molecular ions. This project is part of the excellence initiative of the DFG (MAP) and financial support of MPG and IMPRS-APS is acknowledged.

MO 13.20 Di 16:30 VMP 8 Foyer

**Scanning technique and phase-stability in coherent 2D spectroscopy** — ULRIKE SELIG, FLORIAN LANGHOJER, FRANK DIMLER, TATJANA LÖHRIG, CHRISTOPH SCHWARZ, ●BJÖRN GIESEKING, and

TOBIAS BRIXNER — Institut für Physikalische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

We have recently introduced an inherently phase-stable setup for coherent two-dimensional (2D) spectroscopy using only conventional optics [1]. In this contribution we discuss the underlying principle that ensures its stability, the exclusive manipulation of pulse pairs. We explain the technique of measuring the third-order optical response, the scanning procedure allowing for adequate variation of the time delays between the three pulses, and the analysis of the recorded data via Fourier evaluation.

[1] U. Selig, F. Langhojer, F. Dimler, T. Löhrig, C. Schwarz, B. Gieseck, and Tobias Brixner, *Opt. Lett.* **33**, 2851-2853 (2008)

MO 13.21 Di 16:30 VMP 8 Foyer

**Local control of population transfer in molecules under noise** — ●ROBERT KRITZER and VOLKER ENGEL — Institut für Physikalische Chemie, Am Hubland, 97074 Würzburg

We investigate the laser induced population transfer between electronic states of Na<sub>2</sub> molecules which are subject to perturbations by noise. In a former paper [1] it was shown, that within the formalism of *Local Control Theory* laser fields can be constructed which are able to selectively transfer population from the electronic ground to a target excited electronic state. These studies assumed an unperturbed molecular motion. Here, we address the question in how far the efficiency of the control process is reduced by additional perturbations. Therefore, we employ a stochastic Schrödinger equation including a noise-term in the Hamiltonian [2].

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

[2] K. P. Singh, J. M. Rost, *Phys. Rev. A* **76**, 063403 (2007).

MO 13.22 Di 16:30 VMP 8 Foyer

**On the divergence of time-dependent perturbation theory applied to the laser-induced population transfer in molecules** — ●KLAUS RENZIEHAUSEN and VOLKER ENGEL — Institut für Physikalische Chemie, Am Hubland, 97074 Würzburg

Population transfer between electronic molecular states can be effectively induced via the interaction with shaped laser pulses. Regarding a numerical example, it is demonstrated that the scheme usually employed in (perturbative) numerical calculations might lead to divergences. Analytical considerations show, that the occurring error for a calculation of the norm can be de-composed into two parts. The first one is a small numerical error, which is controllable by minimization of the time-propagation step, whereas the second part, which can cause divergences, is related to the order of the perturbative expansion. An improved scheme is proposed in which the first part carrying the numerical error disappears.

MO 13.23 Di 16:30 VMP 8 Foyer

**Nonadiabatic Quantum Dynamics and Laser Control in of Br<sub>2</sub> in Solid Argon** — ●OLIVER KÜHN<sup>1</sup>, ANTONIO ACCARDI<sup>2</sup>, and ALEXANDER BOROWSKI<sup>2</sup> — <sup>1</sup>Institut für Physik, Universität Rostock — <sup>2</sup>Institut für Chemie und Biochemie, Freie Universität Berlin

In this presentation the focus will be on some general issues concerning the treatment of laser driven nonadiabatic multidimensional quantum dynamics of complex systems. As a specific example Br<sub>2</sub> occupying a double substitutional site in solid Ar is discussed [1]. It is shown how the complexity can systematically be reduced by introducing a Cartesian Reaction Surface Vibronic Coupling model [2,3]. The latter is suited for a quantum dynamics study employing the multiconfiguration time-dependent Hartree approach [4]. In the analysis special emphasis is paid to the role of conical intersections which are responsible for the B to C predissociation. Finally, active control of the nonadiabatic dynamics using shaped laser pulses is demonstrated [5].

[1] M. Bargheer et al., in O. Kühn, L. Wöste (eds.) "Analysis and Control of Ultrafast Photoinduced Reactions", Springer, Heidelberg, 2007, p. 257. [2] A. Borowski, O. Kühn, *Theor. Chem. Acc.* **117**, 521 (2007). [3] A. Borowski, O. Kühn, *J. Photochem. Photobiol. A*, **190**, 169 (2007). [4] A. Borowski, O. Kühn, *Chem. Phys.* **347**, 523 (2008). [5] A. Accardi, A. Borowski, O. Kühn, in preparation.

MO 13.24 Di 16:30 VMP 8 Foyer

**Implementation of the von Neumann basis in a genetic algorithm** — ●STEFAN RUETZEL<sup>1</sup>, CHRISTOPH STOLZENBERGER<sup>1</sup>, SUSANNE FECHNER<sup>1</sup>, FRANK DIMLER<sup>1</sup>, DAVID J. TANNOR<sup>2</sup>, and TOBIAS BRIXNER<sup>1</sup> — <sup>1</sup>Institut für Physikalische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany — <sup>2</sup>Department

of Chemical Physics, Weizmann Institute of Science, 76190 Rehovot, Israel

The representation of ultrashort laser pulses in phase space, i.e. in a joint-time-frequency representation, is a suitable way to simultaneously show both temporal and spectral features. Especially when using adaptive quantum control in combination with pulse shaping this type of representation can help to identify and to interpret the main features of the often complex structured pulses.

Recently we introduced the von Neumann representation based on a paper by John von Neumann and showed first experimental implementations of this technique. Here we present in more detail how to define and characterize ultrashort laser pulses in the von Neumann picture. We integrated the von Neumann representation into a genetic algorithm (GA) by encoding the temporal and spectral position as well as the amplitude and the phase of the von Neumann pulses into the GA gene values. The practicability of this basis was shown by simulations and the generated pulses were analyzed by spectral interferometry (SI).

MO 13.25 Di 16:30 VMP 8 Foyer

**Ultra-broadband single-beam CARS spectroscopy probing CH-vibrations at 3000 cm<sup>-1</sup>** — ●CHRISTINA MÜLLER<sup>1</sup>, SANGAM CHATTERJEE<sup>2</sup>, BERNHARD VON VACANO<sup>3</sup>, and MARCUS MOTZKUS<sup>1</sup> — <sup>1</sup>FB Chemie, Philipps-Universität Marburg, Hans-Meerwein-Strasse, D-35043 Marburg, Germany — <sup>2</sup>FB Physik, Philipps-Universität Marburg, Renthof 5, D-35032 Marburg, Germany — <sup>3</sup>Polymer Physics, BASF SE, Carl-Bosch-Str. 38, D-67056 Ludwigshafen, Germany

In order to probe a complete coherent anti-Stokes Raman scattering (CARS) spectrum of more than 3000 cm<sup>-1</sup> with a single-beam excitation, pulses having an extreme bandwidth are required. In this contribution we demonstrate the extension of the combination of ultra-broadband pulses created in a photonic crystal fibre (PCF) and pulse shaping for non-linear coherently controlled spectroscopy by using two pulse shapers. The first shaper compresses the initial pulse from the laser source to its Fourier limit then acting as pump for the PCF. White light generated within the fibre is characterised and pre-compressed using SHG FROG traces obtained after the beam passed the second pulse shaper. Correction of pulse distortion, especially due to the microscope objectives needed to create CARS frequencies, is accomplished by maximisation single-beam CARS signal using the second shaper again in a closed-loop optimisation scheme. Spectral resolution in any single-beam measurement is as well achieved with the second shaper through sinusoidal phase functions. Pulses as short as 12 fs have been used successfully to probe molecular vibrations corresponding to CH-bonds settled in a range of more than 3000 cm<sup>-1</sup>.

MO 13.26 Di 16:30 VMP 8 Foyer

**Kontrolle der ISC-Rate von Farbstoffen in Lösung** — ●JOHANNES SCHNEIDER<sup>1</sup>, MATTHIAS WOLLENHAUPT<sup>1</sup>, THOMAS BAUMERT<sup>1</sup>, CHRISTIAN BURMESTER<sup>2</sup> und RÜDIGER FAUST<sup>2</sup> — <sup>1</sup>Universität Kassel, Institut für Physik und CINSaT, Heinrich-Plett-Str. 40, D-34132 Kassel — <sup>2</sup>Universität Kassel, Institut für Chemie und CINSaT, Heinrich-Plett-Str. 40, D-34132 Kassel

Ziel dieses Projekts ist es, die Intersystem Crossing (ISC) Rate von Farbstoffmolekülen mittels fs-Pulsformung zu beeinflussen. Vor allem die Wahl eines passenden Farbstoffmoleküls, die Präparation eines über lange Zeit konstanten ISC-Signals und die eigentliche Messung der ISC-Rate stellen dabei große Herausforderungen dar. Es wird das physikalische System sowie der experimentelle Aufbau präsentiert, mit dem ein geeignetes Rückkopplungssignal für die Pulsformungsroutine gefunden wurde.

MO 13.27 Di 16:30 VMP 8 Foyer

**Spectroscopy of single low-light harvesting 2 complexes from *Rps. palustris* 2.1.6** — ●RALF KUNZ<sup>1</sup>, TATAS H.P. BRODOSUDARMO<sup>2</sup>, ALASTAIR T. GARDINER<sup>2</sup>, VLADIMIRA MOULISOVA<sup>2</sup>, RICHARD J. COGDELL<sup>2</sup>, and JÜRGEN KÖHLER<sup>1</sup> — <sup>1</sup>Experimental Physics IV, University of Bayreuth — <sup>2</sup>Department of Biochemistry & Molecular Biology, Faculty of Biomedical & Life Sciences, University of Glasgow

Polarization dependent fluorescence-excitation spectra of single low-light (LL) harvesting 2 complexes from *Rps. palustris* strain 2.1.6 have been recorded at low temperature (1.4 K). The recorded spectra feature three main absorption bands around 800 nm, 820 nm, and 850 nm, respectively. On the basis of a structural model that assumes 9  $\alpha\beta$  BChl dimers and a mixed apoprotein composition the spectra have been simulated. The best agreement between experiment and simulation is achieved for a model that considers 6  $\alpha$ -bound B820-like BChls

and 12 B850-like BChls that are arranged in  $C_3$  symmetry.

MO 13.28 Di 16:30 VMP 8 Foyer

**Raman Study of AKR/J Mice Spleen at Different Excitation and Bleaching Profiles, and of Hormonal and Tumorigenic Changes in Hamsters** — ●PATRICE DONFACK, ALEXANDER LERCHL, and ARNULF MATERNY — Jacobs University Bremen, Germany

We present Raman spectroscopic studies of transgenic AKR/J mouse spleen tissue under green and red excitation, and of hamster liver, thymus, and testes tissue under red excitation, in combination with multivariate analysis. With green excitation, healthy and cancerous spleen showed slight changes in the intensity ratio  $I_{1672}/I_{1450}$ , different amide III bands, reduced intensity of the phenylalanine (Phe) band, and especially stronger nucleic acid (*e.g.* DNA:  $1085\text{ cm}^{-1}$ ) bands in tumors and a double fine structure at  $1606$  and  $1639\text{ cm}^{-1}$  in different aspect ratios. Under red excitation, the intensity of the Phe band drops notably in tumors and could be used for both differentiation and grading. Using different excitations, we show that some characteristic features could only be resolved for certain wavelengths. Moreover, the fluorescence bleaching time profile under green excitation provided insight into the actual bleaching effect and the retained aspect ratio of the double fine structure at  $1606$  and  $1639\text{ cm}^{-1}$  is consistently correlated with tumorigenicity. Hamsters subjected to seasonal changes of day/night ratios experience fur color change, and can show enlarged testes in short day periods. With Raman spectra of liver, thymus, and especially of testes tissue, matched with short and long day hamsters, we hypothesize on eventual hormonal changes, and a Raman indication of tumorigenesis in short day hamsters with enlarged testes.

MO 13.29 Di 16:30 VMP 8 Foyer

**VIS Raman Spectroscopy for the Classification of and Adulteration Detection in Vegetable Oils** — ●RASHA HASSANEIN, PATRICE DONFACK, and ARNULF MATERNY — Jacobs University Bremen, Germany

Raman spectroscopy with visible light (VIS) excitation in combination with multivariate analysis is an efficient technique for the characterization of olive oil; it also can be used for an early detection of oil adulteration. Major advantages are, (i) it requires no sample preparation, (ii) it is a rapid and nondestructive tool, and (iii) when combined with *e.g.* fiber optics, it can be used directly in industrial processes. In our work, we have demonstrated the potential capabilities of dispersive Raman spectroscopy using VIS excitation in combination with appropriate chemometric methods for the investigation and identification of different vegetable oils. Moreover, the adulteration of olive oil with similar oils such as sunflower oil – which is a common adulterant for olive oil because of its high oleic content – could be detected even for very low concentrations; detection limits down to  $500\text{ ppm}$  of the adulterant have been achieved without considerable effort. To our knowledge, the advantages of VIS Raman spectroscopy were up to now not utilized for olive oil characterization. However, due to the VIS excitation increased signal intensities result for components at low concentration (*e.g.* for carotenoids); but also in general stronger Raman signals can be expected due to the  $\nu^4$ -dependence of the scattering process. The latter effect results in very short measuring times.

MO 13.30 Di 16:30 VMP 8 Foyer

**Optically ‘Dark’ States of Xanthophylls in the Major Plant Light-Harvesting Complex Studied by Femtosecond Two-Photon Excitation Spectroscopy** — ●ALEXANDER BETKE<sup>1</sup>, BERND VOIGT<sup>1</sup>, HEIKO LOKSTEIN<sup>1,2</sup>, and RALF MENZEL<sup>1</sup> — <sup>1</sup>Institut für Physik und Astronomie / Photonik, Universität Potsdam — <sup>2</sup>Institut für Biochemie und Biologie, Universität Potsdam

Carotenoids (Xanthophylls) play crucial roles in photosynthesis: *i.e.*, as accessory light-harvesting pigments and photoprotectors. To understand these functions it is vital to know the energetic positions of their lowest excited singlet states,  $S_1$  ( $2^1A_g^-$ ). Since one-photon absorption is forbidden for the  $S_0$  ( $2^1A_g^-$ )  $\rightarrow$   $S_1$  ( $2^1A_g^-$ ) transition, the xanthophyll  $S_1$  state is optically ‘dark’ and cannot be readily investigated by conventional spectroscopic techniques. This transition, however, is two-photon allowed. Two-photon absorption (TPA) of tunable near-infrared fs-pulses is used to investigate the role of the xanthophylls ‘dark’ states in excitation energy transfer (EET) and dissipation in light-harvesting complexes. TPA can either be monitored by chlorophyll fluorescence (provided that EET onto chlorophyll occurs) or by probing transient absorption changes. A detailed study of two-photon-excitation of the plant major light-harvesting complex (LHC II) containing different xanthophyll-cycle pigment complements

(violaxanthin, zeaxanthin) and of these pigments in solution will be given using both techniques. Implications for the photoprotective non-photochemical quenching (NPQ) mechanism will be discussed. This research is supported by the DFG (SFB 429, TP A2).

MO 13.31 Di 16:30 VMP 8 Foyer

**Anion molecule reaction dynamics** — ●MARTIN STEI<sup>1</sup>, SEBASTIAN TRIPPEL<sup>1</sup>, PETR HLAVENKA<sup>1</sup>, RICO OTTO<sup>1</sup>, MATTHIAS WEIDEMÜLLER<sup>2</sup>, and ROLAND WESTER<sup>1</sup> — <sup>1</sup>Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg — <sup>2</sup>Physikalisches Institut, Universität Heidelberg, Albert-Überle-Str. 3-5, 69120 Heidelberg

Anion-molecule reaction processes are known for their rich reaction dynamics, caused by a complex potential energy surface. We have carried out the first kinematically complete study of the  $S_N2$  reaction of  $\text{F}^-$  and  $\text{Cl}^- + \text{CH}_3\text{I}$  using crossed molecular beam imaging. Different reaction mechanisms were observed as a function of collision energy [1].

We report the improvement of the velocity imaging spectrometer, characterized by REMPI-spectroscopy of  $\text{NH}_3$ . For improved 3D imaging we are currently adding a direct time-of-flight measurement. We have imaged the alignment and dissociation dynamics of  $\text{CH}_3\text{I}$  in a strong laserfield by using nanosecond pulses. We will extend our research to investigating orientation effects in ion molecule reactions.

[1] J. Mikosch *et al.*, Science **319**, 183 (2008)

MO 13.32 Di 16:30 VMP 8 Foyer

**Dissociative electron capture in collisions of  $\text{Ar}^{8+}$  and  $\text{CO}_2$**  — ●NADINE NEUMANN, JASMIN TITZE, LOTHAR SCHMIDT, ACHIM CZASCH, OTTMAR JAGUTZKI, HORST SCHMIDT-BÖCKING und REINHARD DÖRNER — Institut für Kernphysik, Goethe Universität Frankfurt, Max-von-Laue Str. 1, 60438 Frankfurt am Main, Germany

We are using the Cold Target Recoil Ion Spectroscopy (COLTRIMS) to investigate the break up of  $\text{CO}_2$  in impact processes with slow highly charged ions. While the slow highly charged ions passes the  $\text{CO}_2$  molecule electron capture into the projectile causes a conformation change of the  $\text{CO}_2$  molecule. With the COLTRIMS set up we are able to measure the  $4\pi$  solid angle in momentum space of the dissociating ion fragments. The motivation for this experiment is to ascertain the change of the  $\text{CO}_2$  molecule conformation.

MO 13.33 Di 16:30 VMP 8 Foyer

**Untersuchung der Reaktionsdynamik bei der Transferionisation an Heliumdimeren** — JASMIN TITZE, ●FLORIAN TRINTER, MARKUS WAITZ, HONG-KEUN KIM, M. SCHÖFFLER, S. KIRSCHNER, K. KREIDI, N. NEUMANN, M. ODENWELLER, B. ULRICH, J. VOIGTSBERGER, R. WALLAUER, T. JAHNKE, A. CZASCH, LOTHAR SCHMIDT, O. JAGUTZKI, REINHARD DÖRNER und H. SCHMIDT-BÖCKING — Institut für Kernphysik Frankfurt, Deutschland

Heliumdimere stellen das am weitesten gebundene atomare System dar. In Stößen mit  $\text{He}^{2+}$  bei Projektilenergien von  $150\text{ keV/u}$  wurde die Abstandsverteilung sowie die Zerfallsdynamik der Transferionisation  $\text{He}^{2+} + \text{He}_2 \rightarrow \text{He}^+ + \text{He}^+ + \text{e}^-$  mittels der COLTRIMS-Technik (Cold Target Recoil Ion Momentum Spectroscopy) untersucht. Hierbei konnten drei Zerfallsmechanismen nachgewiesen werden.

MO 13.34 Di 16:30 VMP 8 Foyer

**Suche nach Unterschieden in der Ionisationsdynamik von  $\text{H}_2$  und  $\text{D}_2$**  — ●MARKUS WAITZ<sup>1</sup>, FLORIAN TRINTER<sup>1</sup>, JASMIN TITZE<sup>1</sup>, MARKUS S. SCHÖFFLER<sup>2</sup>, MATTHIAS KÜHNEL<sup>1</sup>, OTTMAR JAGUTZKI<sup>1</sup>, HONG-KEUN KIM<sup>1</sup>, LOTHAR PH. H. SCHMIDT<sup>1</sup>, HORST SCHMIDT-BÖCKING<sup>1</sup> und REINHARD DÖRNER<sup>1</sup> — <sup>1</sup>Institut für Kernphysik, Max-von-Laue-Straße 1, 60438 Frankfurt am Main, Goethe-Universität Frankfurt am Main, Deutschland — <sup>2</sup>Berkeley-Lab, 1 Cyclotron Rd, Berkeley CA 94720, USA

Auf der atomaren Größenskala wird jegliche Wechselwirkung von der elektromagnetischen Kraft dominiert, absolute und differentielle Wirkungsquerschnitte werden als isotopenunabhängig angesehen.

Im Gegensatz dazu stellten Cooper und Mitarbeiter Unterschiede in den Wirkungsquerschnitten quasi-elastischer Elektronen-Streuprozesse an  $\text{H}_2$ -,  $\text{D}_2$ - und  $\text{HD}$ -Gasen fest [1]. Diesen Ergebnissen nach wäre der zugehörige geometrische Wirkungsquerschnitt kleiner als erwartet.

In vorangegangenen Experimenten konnten wir zeigen, dass in Kollisionen von  $\text{He}^+$ -Projektile mit einem  $\text{He}$ -Target die gleichzeitige Projektil- und Targetionisation durch zwei verschiedene Prozesse geschieht: Elektron-Elektron- und Elektron-Kern-Wechselwirkung. In

Abhängigkeit von der Stoßenergie dominiert einer dieser Prozesse [2]. In unserem Experiment nutzen wir die COLTRIMS-Technik, um diese Ionisationsdynamik in Stößen von He<sup>+</sup>-Projektilen mit einer Mischung aus H<sub>2</sub>- und D<sub>2</sub>-Molekülen zu vermessen. Ergebnisse der Messung werden vorgestellt und diskutiert.

MO 13.35 Di 16:30 VMP 8 Foyer

**X-ray absorption spectroscopy of size selected protonated water clusters** — ●JÜRGEN PROBST<sup>1</sup>, KONSTANTIN HIRSCH<sup>1</sup>, ANDREAS LANGENBERG<sup>1</sup>, ROBERT RICHTER<sup>1</sup>, JOCHEN RITTMANN<sup>1</sup>, MARLENE VOGEL<sup>1</sup>, VICENTE ZAMUDIO-BAYER<sup>1</sup>, THOMAS MÖLLER<sup>1</sup>, PHILIPPE WERNET<sup>2</sup>, BERND VON ISSENDORFF<sup>3</sup>, and TOBIAS LAU<sup>1</sup> — <sup>1</sup>Technische Universität Berlin, Institut für Optik und Atomare Physik, EW 3-1, Hardenbergstraße 36, D-10623 Berlin — <sup>2</sup>BESSY GmbH, Albert-Einstein-Straße 15, D-12489 Berlin — <sup>3</sup>Universität Freiburg, Fakultät für Physik, Stefan-Meier-Straße 21, D-79104 Freiburg

The electronic and geometric structures of size selected protonated water clusters are studied with X-ray absorption spectroscopy at the oxygen K-edge. Transitions from oxygen 1s electrons into unoccupied molecular orbitals are particularly sensitive to hydrogen bonding of water molecules and give information on the local structure of protonated water clusters. We have recently set up a water cluster source compatible with our liquid nitrogen cooled ion trap for core level spectroscopy. Preliminary results on size selected H<sup>+</sup>(H<sub>2</sub>O)<sub>n</sub> (n=4-14) clusters indicate a size dependent shift of the resonant x-ray absorption lines. Spectral signatures in this size range are closer to gas-phase water molecules or the ice Ih surface than to liquid water. We will present the experimental setup and discuss our results in comparison to theory and experiments on gas phase water molecules, liquid water, and ice.

MO 13.36 Di 16:30 VMP 8 Foyer

**Size and Shape Dependence of the Optical Properties of Ideal Diamond Clusters - Diamondoids** — ●LASSE LANDT<sup>1</sup>, DAVID WOLTER<sup>1</sup>, MATTHIAS STAIGER<sup>1</sup>, JEREMY DAHL<sup>2</sup>, ROBERT CARLSON<sup>2</sup>, THOMAS MÖLLER<sup>1</sup>, and CHRISTOPH BOSTEDT<sup>1</sup> — <sup>1</sup>Technische Universität Berlin, Germany — <sup>2</sup>MolecularDiamond Technologies, Richmond (CA), USA

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

We have investigated highest occupied and lowest unoccupied states as well as optical absorption across the gap for clusters ranging in size from one six diamond crystal cages. The combination of these three investigations paints a comprehensive picture of their electronic structure. All experiments have been performed in the gas phase reproducing the same idealized boundary conditions of interaction-free and neutral clusters typically assumed in theoretical investigations. We find that the lowest unoccupied states do not show any dependence on particle size. The highest occupied states, however, show strong size but only minor isomeric dependencies. These findings are explained with the localization of the lowest unoccupied states on the surface and the highest occupied states in the core of the cluster. The absorption measurements across the gap in the VUV energy regime reveal strong changes of the spectra with the particle shape and symmetry.

MO 13.37 Di 16:30 VMP 8 Foyer

**Influence of functionalization on the electronic structure of ideal nanodiamonds - diamondoids** — ●DAVID WOLTER<sup>1</sup>, MATTHIAS STAIGER<sup>1</sup>, LASSE LANDT<sup>1</sup>, WITOSLAW KIELICH<sup>2</sup>, JEREMY E. DAHL<sup>3</sup>, ROBERT CARLSON<sup>3</sup>, THOMAS MÖLLER<sup>1</sup>, and CHRISTOPH BOSTEDT<sup>1</sup> — <sup>1</sup>Technische Universität Berlin — <sup>2</sup>Universität Kassel — <sup>3</sup>MolecularDiamond Technologies

Nanodiamonds, so called diamondoids are carbon clusters with perfect bulk diamond structure and complete hydrogen passivation. Diamondoids can be perfectly size-selected and isomer resolved even in their neutral state. This has made possible a variety of investigations on the size and shape dependence of their electronic structure and optical properties. Functionalization of diamondoids allows including them into solid-state devices. We studied the influence of functionalization, by changing the size of the functionalized diamondoid, by variation of the position of the functional group, and by using different functional groups. Our results show that functionalization can be used to tune the diamondoids HOMO - LUMO gap and to modify their electronic structure.

MO 13.38 Di 16:30 VMP 8 Foyer

**A Molecular Synchrotron** — ●P. C. ZIEGER<sup>1</sup>, C. E. HEINER<sup>1</sup>, A. J. A. VAN ROIJ<sup>2</sup>, H. L. BETHLEM<sup>1,3</sup>, S. Y. T. VAN DE MEERAKKER<sup>1</sup>, and G. MEIJER<sup>1</sup> — <sup>1</sup>Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany — <sup>2</sup>Radboud University, Nijmegen, The Netherlands — <sup>3</sup>Laser Centre Vrije Universiteit, Amsterdam, The Netherlands

With the so-called Stark decelerator it has been shown that it is possible to produce a beam of cold neutral polar molecules with a tunable velocity that are well suited for molecular beam scattering studies[1]. Molecular storage rings offer particularly interesting prospects for these kind of scattering experiments. In principle, a storage ring allows the confinement of multiple packets of molecules on a circle that repeatedly interact. A storage ring that consists of two hexapole half-rings that are separated by a small gap has been developed[2]. By appropriately switching the voltages as the molecules pass through the gaps, the molecular packet can be kept together as a compact bunch as it revolves around the ring. The broken symmetry of the ring also allows the injection of multiple packets of molecules. We will present an improved version of a molecular synchrotron that consists of 40 straight hexapoles, that allows the simultaneous confinement of 40 molecular packets. These packets can be made to interact repeatedly at well defined times and positions as they revolve the ring. The synchrotron can store these either collinear or counter propagating molecules for times up to seconds, significantly increasing the sensitivity of molecular collision experiments. [1] J. J. Gilijamse et al., *Science*, **313**, 5793, 1617-1620 (2006), [2] Heiner et al., *Nature Physics*, **3**, 115-118 (2007).

MO 13.39 Di 16:30 VMP 8 Foyer

**Cold molecular anions in a multipole rf trap** — ●RICO OTTO<sup>1</sup>, PETR HLAVENKA<sup>1</sup>, SEBASTIAN TRIPPEL<sup>1</sup>, MARTIN STEI<sup>1</sup>, MATTHIAS WEIDEMÜLLER<sup>2</sup>, and ROLAND WESTER<sup>1</sup> — <sup>1</sup>Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg — <sup>2</sup>Physikalisches Institut, Universität Heidelberg, Albert-Überle-Str. 3-5, 69120 Heidelberg

When studying interaction processes of stored cold anions only few quantum states of the investigated systems are populated. Energies on the scale of rotational levels become dominant at temperatures of only a few Kelvin. We study slow collisions and laser induced processes of cold anions in a 22pole radio frequency trap. Proton transfer from H<sub>2</sub> to NH<sub>2</sub><sup>-</sup> has been found to show unexpected low temperature characteristics in the reaction rate coefficient below 20 K [1]. Measurements of the absolute photodetachment cross section [2] have been carried out for O<sup>-</sup>, a calibration standard for photodetachment, and for OH<sup>-</sup> [3]. The OH<sup>-</sup> photodetachment cross section shows no temperature dependence in the range between 8 - 300K. A new level of accuracy has been reached using a novel 2D tomography scanning technique. This technique allows to image the ion distribution in the 22pole trap, probing the trapping potential.

[1] R. Otto *et al.*, *Phys. Rev. Lett.* **101**, 063201 (2008)

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

[3] P. Hlavenka *et al.*, submitted

MO 13.40 Di 16:30 VMP 8 Foyer

**Spectroscopy of Rb<sub>2</sub> triplet molecules** — CHRISTOPH STRAUSS<sup>1</sup>, TETSU TAKEKOSHI<sup>1</sup>, ●FLORIAN LANG<sup>1</sup>, RUDOLF GRIMM<sup>1,2</sup>, and JOHANNES HECKER DENSCHLAG<sup>1</sup> — <sup>1</sup>Institut für Experimentalphysik und Zentrum für Quantenphysik, Universität Innsbruck — <sup>2</sup>Institut für Quantenoptik und Quanteninformation der Österreichischen Akademie der Wissenschaften

We have recently reported [1] the production of an ultracold gas of tightly bound Rb<sub>2</sub> triplet molecules in the rovibrational ground state, close to quantum degeneracy. This was achieved by optically transferring weakly bound Rb<sub>2</sub> molecules to the absolute lowest level of the  $a^3\Sigma_u^+$  triplet electronic ground state potential. The implementation of such a transfer requires detailed knowledge about the molecular level structure, which previously was experimentally unexplored.

Here we present detailed results from Raman spectrometry of the  $a^3\Sigma_u^+$  potential. We have surveyed the progression of vibrational levels from the last bound state ( $v = 40$ ) to the vibrational ground state  $v = 0$ . We have further resolved the hyperfine structure of the different vibrational levels and find good agreement with close-coupled channel model calculations.

[1] F. Lang *et al.*, *Phys. Rev. Lett.* **101**, 133005 (2008)

MO 13.41 Di 16:30 VMP 8 Foyer

**Stark effect of the system B<sup>1</sup>Π - X<sup>1</sup>Σ<sup>+</sup> in NaK** — ●ANDREAS GERDES, HORST KNÖCKEL, and EBERHARD TIEMANN — Institut

für Quantenoptik, Gottfried Wilhelm Leibniz Universität Hannover, Welfengarten 1, 30167 Hannover

Ultracold dipolar molecular gases have gained great interest in recent years. We studied NaK by Fourier-transform spectroscopy in a heat-pipe setup [1] and prepared in our new molecular beam apparatus by two lasers with a coherent  $\Lambda$  scheme for population transfer selected rovibrational levels of the molecular ground state for investigating the Stark effect of the heteronuclear molecule NaK. Optimization of the transfer schemes was necessary to ensure good S/N ratio. For a description of the Stark splitting not only the molecular Stark effect of the absolute ground state  $X^1\Sigma^+$  of the molecule, but also that of the excited state  $B^1\Pi$  has to be taken into account. The progress of our investigation in this direction will be shown. A comparison with theoretical predictions of the dependence of the electric dipole moment function on the vibrational quantum number [2] should become possible.

[1] A. Gerdes *et al.*, *Eur. Phys. J. D* **49** 67 (2008)

[2] M. Aymar and O. Dulieu, *J. Chem. Phys.* **122** 204302 (2005)

MO 13.42 Di 16:30 VMP 8 Foyer

**Towards spectroscopic analysis of water clusters in a planar multipole ion trap** — ●CHRISTIAN GREVE<sup>1</sup>, MICHAEL KRÖNER<sup>2</sup>, SEBASTIAN TRIPPEL<sup>1</sup>, PETER WOIAS<sup>2</sup>, ROLAND WESTER<sup>1</sup>, and MATTHIAS WEIDEMÜLLER<sup>1</sup> — <sup>1</sup>Institut für Physik, Universität Freiburg — <sup>2</sup>Institut für Mikrosystemtechnik, Universität Freiburg

Charged water clusters especially the protonated water clusters are one of the most extensively studied cluster ions in the gas phase. They play a crucial role in various systems such as in aqueous solutions, in the chemistry of the ionosphere as well as in dense interstellar clouds. Despite numerous efforts, questions concerning the spatial cluster structure and the explanation of the anomalously high proton mobility in aqueous surroundings are not completely solved [1].

To approach these questions we use a supersonic expansion source with pulsed electron bombardement for creating the water clusters which are then loaded into a biplanar multipole chip trap [2]. Analysis after storage is accomplished by time of flight measurements. In cooperation with the University of Bochum we will perform high resolution vibrational predissociation spectroscopy on the stored cluster ions. The presentation will focus on the present stage of the experiment especially on creation and storage properties of the clusters. Moreover we will give an insight into the micro system fabrication technologies involved in the production of the chip trap.

[1] H. Chang *et al.*, *Int. Rev. Phys. Chem.* **24**, 553 (2005)

[2] M. Debatin *et al.*, *Phys. Rev. A* **77**, 033422 (2008)

MO 13.43 Di 16:30 VMP 8 Foyer

**Improved setup of a rotating nozzle for producing slow and cold molecules** — ●MATTHIAS STREBEL, TIM EICHHORN, MARCEL MUDRICH, and FRANK STIENKEMEIER — Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg, Germany

In order to study reactive and non reactive collisions between atoms and molecules at very low scattering energies we plan to combine a magneto-optical trap (MOT) for ultracold lithium atoms with a setup for producing beams of cold molecules at low velocities in the laboratory frame. A slow molecular beam is produced with an improved setup by means of a supersonic expansion from a rapidly rotating nozzle.

Technical details of the device as well as the results of first measurements will be presented. An electrostatic quadrupole guide is implemented in order to efficiently transfer the molecules via the Stark effect into the detection region.

MO 13.44 Di 16:30 VMP 8 Foyer

**Manipulating large neutral molecules with electric fields** — ●FRANK FILSINGER<sup>1</sup>, JOCHEN KÜPPER<sup>1</sup>, KIRSTIN WOHLFART<sup>1</sup>, UN-DINE ERLEKAM<sup>1</sup>, GERT VON HELDEN<sup>1</sup>, GERARD MEIJER<sup>1</sup>, JONAS L. HANSEN<sup>2</sup>, JENS H. NIELSEN<sup>2</sup>, LOTTE HOLMEGAARD<sup>2</sup>, IFTACH NEVO<sup>2</sup>, JOCHEN MAURER<sup>2</sup>, and HENRIK STAPELFELDT<sup>2</sup> — <sup>1</sup>Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany — <sup>2</sup>Århus University, Århus, Denmark

It is well-known that polar molecules can be manipulated using strong electric fields. Many techniques have been developed for the manipulation of small molecules in low-field-seeking quantum states. However, application of these techniques to large molecules is not straightforward, because, for larger molecules, all states are high-field seeking at the relevant electric field strengths.

In order to spatially focus molecules in high-field seeking quantum states, one has to use alternating gradient (dynamic) focusing [1]. This method has been successfully applied, for instance, for the alternating gradient deceleration of benzonitrile [2] and for the conformer selection of 3-aminophenol in an  $m/\mu$ -selector [3]. Alternatively also static electric fields can be exploited for quantum state and conformer selection.

Here we will compare the different approaches to manipulate large neutral molecules with electric fields and discuss applications of conformer (and quantum-state) selected molecules.

[1] H.L. Bethlem *et al.*, *J. Phys. B* **39** (2006), R263.

[2] K. Wohlfart *et al.*, *Phys. Rev. A* **77**(3), (2008), 031404(R)

[3] F. Filsinger *et al.*, *Phys. Rev. Lett.* **100**, (2008), 133003

MO 13.45 Di 16:30 VMP 8 Foyer

**Stark decelerated SO<sub>2</sub> for dissociation and collision studies** — ●OLEG BUCICOV<sup>1</sup>, EBERHARD TIEMANN<sup>1</sup>, and CHRISTIAN LISDAT<sup>2</sup> — <sup>1</sup>Institut für Quantenoptik, Leibniz Universität Hannover — <sup>2</sup>Physikalisch-Technische Bundesanstalt, Braunschweig

We present a Stark decelerator for low-field-seeking states with 326 stages, with which we succeeded in decelerating SO<sub>2</sub> molecules to the velocity of about 50 m/s [1]. With this decelerator it should be possible to bring the relatively heavy SO<sub>2</sub> molecules to a standstill and to trap them electrostatically.

The state specific predissociation at the threshold of decelerated SO<sub>2</sub> molecules, prepared in a first excitation step using a frequency-doubled pulsed dye laser, results in producing cold SO and O fragments. The detection of the molecular fragment SO by means of the (1+1) REMPI technique using a second frequency-doubled pulsed dye laser makes it possible to measure the velocity distribution of the both photofragments.

Previous Stark-effect measurements [2] in our group showed that the dissociation process can be manipulated by an external electric field by shifting the dissociation asymptote relative to the predissociating level. In this way dissociation channels can be opened or closed at will or the velocity of the fragments can be tuned. These opportunities are very attractive for the field of cold molecules and cold chemistry.

[1] O. Bucicov, *Eur. Phys. J. D* **46** 463 (2008).

[2] S. Jung, *J. Phys. B* **39** S1085 (2006).

MO 13.46 Di 16:30 VMP 8 Foyer

**Collisional effects in the formation of cold guided beams of polar molecules** — MICHAEL MOTSCH, CHRISTIAN SOMMER, LAURENS D. VAN BUUREN, MARTIN ZEPPEFELD, ●PEPIJN W.H. PINKSE, and GERHARD REMPE — Max-Planck-Institut für Quantenoptik, Hans-Kopfermann-Str. 1, 85748 Garching, Germany

Electric guiding and velocity filtering produces high fluxes of cold polar molecules [1]. Here, we investigate different aspects of the beam formation. Variation of gas density and, to a lesser extend, temperature in the source results in characteristic changes in the guided beam. These are observed in the velocity distribution of the guided molecules as well as in characteristic electrode voltage dependencies. The behaviour can be understood by taking into account velocity-dependent collisional losses of cold molecules in and near the nozzle. The description including collisional effects clarifies the parameter dependence of the detected signal as measured by a quadrupole mass spectrometer and provides a more detailed understanding of the velocity filtering and guiding process [2].

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

[2] M. Motsch *et al.*, ArXiv:0812.2850

MO 13.47 Di 16:30 VMP 8 Foyer

**Towards Improved Rovibrational Spectroscopy of Cold Trapped HD<sup>+</sup> Ions** — ●TOBIAS SCHNEIDER, BERNHARD ROTH, ULF BRESSEL, INGO ERNSTING, MICHAEL HANSEN, HANNES DUNCKER, SERGEY VASILYEV, ALEXANDER NEVSKY, and STEPHAN SCHILLER — Institut für Experimentalphysik, Heinrich-Heine Universität Düsseldorf, 40225 Düsseldorf

HD<sup>+</sup> ions, the simplest heteronuclear molecules in nature, are interesting systems for precision spectroscopy because of the availability of precise theoretical ab-initio calculations [1]. Promising applications are, for example, improved tests of QED effects in molecules and the possibility to determine the electron-to-proton mass ratio  $m_e/m_p$ .

We describe work towards improved measurements of rovibrational transition frequencies in cold, trapped HD<sup>+</sup> ions, aiming to reach an at least tenfold improvement over our previous measurements [2]. We present recent modifications to our apparatus and measurement procedures, that will ultimately allow (i) deterministic preparation of the

HD<sup>+</sup> ions in their rovibrational ground state, (ii) precise determination of the hyperfine hamiltonian and the Zeeman effect using THz rotational spectroscopy, and (iii) Doppler-free spectroscopy.

[1] V.I. Korobov, *Phys. Rev. A* **74**, 052506 (2006)

[2] J. Koelemeij et al., *Phys. Rev. Lett.* **98**, 173002 (2007)

MO 13.48 Di 16:30 VMP 8 Foyer

**Velocity filtering of a continuous molecular beam in a curved hexapole guide** — •BENJAMIN BERTSCHE, ANDREAS OSTERWALDER, and GERARD MEIJER — Fritz-Haber-Institut, Berlin, Germany

An experiment is presented which extends a method originally intro-

duced by Rangwala et al. (*Phys. Rev. A* **67**, 043406 (2003)): the filtering of slow dipolar molecules from a thermal gas using the strong electric fields from a multipole guide.

While Rangwala et al. used static fields from a curved quadrupole to select molecules below a certain threshold velocity, in our current experiment a curved *hexapole* is employed, and different static and time-dependent electric fields are then used to select molecules with velocities *within a certain range*. The potential state- and velocity selection by this technique are explored using ammonia (both NH<sub>3</sub> and ND<sub>3</sub>), and discussed in comparison with trajectory simulations.