

MO 13: Poster 1: Cold Molecules, Femtosecond Spectroscopy, Molecular Dynamics

Time: Tuesday 16:30–19:00

Location: Poster.IV

MO 13.1 Tue 16:30 Poster.IV

Towards Cold Ion-Radical Chemistry with Magnetically Decelerated Atoms — ●KATRIN DULITZ¹, CHRIS J. RENNICK¹, MICHAEL MOTSCH², HANSJÜRG SCHMUTZ², FRÉDÉRIC MERKT², and TIMOTHY P. SOFTLEY¹ — ¹Department of Chemistry, University of Oxford, Chemistry Research Laboratory, Mansfield Road, Oxford, OX1 3TA, United Kingdom — ²Laboratorium für Physikalische Chemie, ETH Zürich, CH-8093, Switzerland

Zeeman deceleration is an experimental technique in which inhomogeneous, pulsed magnetic fields are used to control the velocity of a supersonic beam. The method is based on the Zeeman interaction between paramagnetic particles and magnetic fields, enabling the deceleration of species like atomic hydrogen or molecular oxygen [1, 2]. We present the design of a 12-stage Zeeman decelerator for hydrogen atoms that can readily be integrated into an existing ion-trap setup [3] using a bent magnetic hexapole guide. This combined Zeeman decelerator - ion trap experiment will allow for experiments on cold ion-radical reactions, e. g., between H atoms and sympathetically cooled CO₂⁺. An extended version of the decelerator will be used for the deceleration of deuterium atoms to study kinetic isotope effects in low-temperature ion-radical reactions. The work will contribute towards the understanding of chemical reactivity in the low-temperature regime and it will provide fundamental tests for chemical reaction theories.

[1] N. Vanhaecke et al., Phys. Rev. A **75**, 031402 (2007). [2] E. Naravicius et al., Phys. Rev. A **77**, 051401 (2008). [3] S. Willitsch et al., Phys. Rev. Lett. **100**, 043203 (2008).

MO 13.2 Tue 16:30 Poster.IV

A centrifuge decelerator for supersonic beams of buffer-gas cooled polar molecules — ●ANDREAS ROHLFES, XING WU, CHRISTIAN SOMMER, SOTIR CHERVENKOV, MARTIN ZEPPENFELD, LAURENS VAN BUUREN, and GERHARD REMPE — Max-Planck-Institut für Quantenoptik, Hans-Kopfermann-Str. 1, D-85748 Garching, Germany

We present a novel and versatile scheme for the production of quasi continuous beams of slow and internally cold polar molecules. We produce internally cold polar molecules by a supersonic expansion from a cryogenic buffer-gas cell, which results in the formation of a continuous and hydrodynamically enhanced beam of longitudinally fast molecules with a narrow velocity distribution. Further, these beams are accepted and guided by a quadrupole electric guide [1] to a centrifuge decelerator. The latter employs the centrifugal potential in a rotating frame to slow down the molecules when they are guided from the periphery to the center. With this deceleration scheme quasi continuous beams of internally cold and slow molecules with longitudinal velocities below 20m/s can be produced. Thus this technique is a suitable source of polar molecules for further experiments, e.g., trapping and subsequent opto-electrical cooling[2].

[1] L.D. van Buuren et al., Phys. Rev. Lett. **102**, 033001 (2009)
[2] M.Zeppenfeld et al., Phys. Rev. A. **80**,041401(R) (2009)

MO 13.3 Tue 16:30 Poster.IV

Reaching for the Ultracold with Polyatomic Molecules — ●BARBARA G.U. ENGLERT, ROSA GLÖCKNER, ALEXANDER PREHN, MARTIN ZEPPENFELD, and GERHARD REMPE — Max-Planck-Institut für Quantenoptik, Hans-Kopfermann-Str. 1, 85748 Garching, Germany

Realizing a general method for cooling polar molecules to ultracold temperatures has been a key area of research over the past decade. The precise control over the molecular degrees of freedom possible at ultracold temperatures combined with the strong dipole-dipole interaction makes ultracold molecules attractive candidates for applications reaching from many-body physics to quantum information science. A highly versatile technique to cool a large variety of polyatomic molecules to the microkelvin regime is opto-electrical cooling [1]. In this general Sisyphus-type cooling scheme the strong interaction of polar molecules with electric fields is exploited to repeatedly remove a large amount of kinetic energy in a single step.

Here we present the first experimental realization of opto-electrical cooling using trapped CH₃F. Trapping is achieved with a microstructured electric trap [1,2] providing a record-long lifetime of over 10s. Vibrational and rotational molecular states are driven using infrared and microwave fields, with homogeneous electric fields in the trap al-

lowing selective addressing of rotational M-sublevels. We achieve a reduction of the molecular temperature from 358 mK to 77 mK, and an increase of the phase-space density by a factor of 7.

[1] M. Zeppenfeld et al., Phys. Rev. A **80**, 041401(R) (2009).
[2] B.G.U. Englert et al., Phys. Rev. Lett, in press (arXiv:1107.2821).

MO 13.4 Tue 16:30 Poster.IV

Laboratory Astrochemistry in a Multipole RF Ion Trap — ●THORSTEN BEST¹, ERIC ENDRES¹, RICO OTTO^{1,2}, and ROLAND WESTER¹ — ¹Inst. f. Ionenphysik u. Angew. Physik, Universität Innsbruck — ²now at Dept. of Chemistry, Univ. of California San Diego

Multipole radio-frequency ion traps provide a favourable environment for laboratory astrochemistry. Collisional cooling with a neutral buffer gas allows to reach the temperature range characteristic for e.g. the interstellar medium, in both the internal and motional degrees of freedom, and to store molecular ions for extended periods of time.

Through coupling of a 22-pole ion trap with a high resolution time of flight mass spectrometer, sensitive measurements of both collision-induced (e.g. reactive) and radiation-induced processes become feasible. We demonstrate the applicability of this experimental setup to several problems in laboratory astrochemistry, including photodetachment [1] and reactions with H₂.

A new perspective for the detection and analysis of gas phase molecules and clusters has recently been opened by the development of novel radiation sources in the Terahertz domain. In combination with powerful astronomical observation tools such as HERSCHEL and ALMA, laboratory THz spectroscopy may lead to the discovery of new species in various astronomical environments. We present our approach towards THz action spectroscopy on cold trapped molecular ions.

[1] T. Best et al., Ap.J. **742**, 63 (2011)

MO 13.5 Tue 16:30 Poster.IV

Detection of Li atoms scattered from a magneto-optical trap by using slow and cold molecular beams — ●BERNHARD RUFF, MATTHIAS STREBEL, MARCEL MUDRICH, and FRANK STIENKEMEIER — Physikalisches Institut, Universität Freiburg, Herman-Herder-Str. 3, D-79104 Freiburg im Breisgau

Slow beams of cold molecules or atoms produced by a rotating nozzle are scattered with magneto-optically trapped Li atoms. Detection of Li by means of surface ionization on a hot ribbon allows to observe elastic and inelastic scattering processes as a function of kinetic energy down to about 1 meV. Technical details regarding the slow molecular beam source, the ultra-cold scattering target and the detection schemes are discussed. Furthermore, first measurements with different atomic and molecular beams are presented.

MO 13.6 Tue 16:30 Poster.IV

Cold molecular collisions with merged beams — ●ANA ISABEL GONZALEZ FLOREZ¹, JANNEKE BLOKLAND¹, HENRIK HAAK¹, NICOLAS VANHAECKE¹, SEBASTIAAN Y T VAN DE MEERAKKER², and GERARD MEIJER¹ — ¹Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany — ²Radboud University Nijmegen, Nijmegen, the Netherlands

Beams of Stark-decelerated molecules have proven to be versatile in studying collisions between atoms and molecules at low collision energies. In these crossed-beam experiments the minimal collision energy was limited to 50 cm⁻¹ by the center-of-mass kinetic energy of the atoms (50 cm⁻¹), hampering the observation of resonances in the scattering cross-section that are predicted to occur at lower energies.

Currently we are developing a set up to collide merged beams of atoms and Stark-decelerated molecules to reach collision energies down to 5 cm⁻¹. We use a curved hexapole to guide Stark-decelerated molecules, such as metastable CO or ND₃, in order to merge them with a beam of He atoms. The He atoms are injected through vacuum with an Even-Lavie valve and cooled down with a cold head. The relative velocity between the two beams can be varied by changing the final velocity of the Stark-decelerated molecules, thus changing the collision energy. Finally, the molecules can be state-selectively detected using (1+1) or (2+1) REMPI, in case of CO or ND₃ respectively.

MO 13.7 Tue 16:30 Poster.IV

Towards precision spectroscopy of laser cooled molecules — ●CORINE MEINEMA, JOOST VAN DEN BERG, KLAUS JUNGSMANN, AERNOUT VAN DER POEL, and STEVEN HOEKSTRA — KVI, University of Groningen, The Netherlands

We aim to use lasercooling to bring alkaline-earth monohalide molecules to ultracold temperatures, in order to perform high-precision spectroscopic tests of fundamental physics. The selected group of molecules is promising because an (almost) closed cycle for lasercooling can be created using a limited number of lasers. By using a Stark decelerator to reduce the average speed of a molecular sample, the required number of scattered photons to reach the ultracold regime (*sim* 100 μ K) is greatly reduced. We are currently working on a supersonic beam of SrF molecules, constructing a Stark-decelerator based on ring electrodes, and setting up the required lasers. Especially interesting to us are the challenges and possibilities of lasercooling molecules in the presence of electric fields. A new generation of precision measurements to probe fundamental interactions and symmetries is possible once such samples of sufficiently cold molecules are available.

MO 13.8 Tue 16:30 Poster.IV

A Molecular Laboratory on a Chip — ●MARK ABEL, SILVIO MARX, SAM MEEK, ANNA ISABEL GONZALEZ FLOREZ, GABRIELE SANTAMBROGIO, and GERARD MEIJER — Fritz-Haber Institut der MPG, 4-6 Faradayweg, 14195 Berlin, Germany

In the past several years, Stark deceleration has proved to be a powerful tool for controlling the translational motion of neutral polar molecules. Chip-based Stark decelerators offer many advantages over the macroscopic designs used previously; among these are relatively low voltage requirements, high field gradients, and tight spatial confinement of polar molecules. In addition, chip-based decelerators offer good optical access for spectroscopic probing and control of the trapped molecules. We show the design of our "molecular lab on a chip," its performance, and the results of rotational- and vibrational spectroscopy on trapped molecules.

MO 13.9 Tue 16:30 Poster.IV

Low energy scattering of Stark-decelerated OH radicals with He atoms with high energy resolution — ●H. CHRISTIAN SCHEWE¹, MORITZ KIRSTE¹, XINGAN WANG¹, LUDWIG SCHARFENBERG¹, NICOLAS VANHAECKE¹, SEBASTIAAN Y.T. VAN DE MEERAKKER², and GERARD MEIJER¹ — ¹Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany — ²Radboud University Nijmegen, Institute for Molecules and Materials, Heyendaalseweg 135, 6525 AJ Nijmegen, The Netherlands

For collision studies of molecules, a Stark decelerator offers the advantage that it produces beams of cold neutral polar molecules with a tunable velocity. A second beam of atoms or molecules will be crossed to study scattering down to collision energies of a few wavenumbers.

We present future experiments where in particular the inelastic scattering of Stark-decelerated and state-selected OH($X^2\Pi_{3/2}$, $J = 3/2, f$) with helium atoms will be carried out [1]. To reach low collision energies down to 10 cm^{-1} a pulsed valve of the Even-Lavie type is mounted on a helium cryostat. The translational velocity and the speed ratio of Helium beams are characterized and their dependence on the temperature, the stagnation pressure and the opening time of the valve are determined. Simulations are presented to show how the resolution of the collision energy can be optimized by bunching of the molecular packet inside the decelerator. We give a perspective on how theoretically predicted scattering resonances of the inelastic cross section might be resolved.

[1] Kirste et al. Phys. Rev. A 82, 4 (2010).

MO 13.10 Tue 16:30 Poster.IV

Systematic analysis of long-range interactions between vibrating polar alkali molecules — ROMAIN VEXIAU, MAXENCE LEPERS, MIREILLE AYMAR, ●OLIVIER DULIEU, and NADIA BOULOUEFA — laboratoire Aimé Cotton, CNRS, Université Paris-Sud, Orsay, France

The determination of the long-range anisotropic interactions between polar alkali molecules is of crucial importance for the achievement of a quantum gas of ultracold polar molecules. In particular, the dispersion coefficient C_6 of the van der Waals interaction depends on the dynamic polarizability of the molecule evaluated at imaginary frequencies, expressed as a sum over all possible radiative transitions of electronic dipole moments. Using a mixture of up-to-date spectroscopic

data and accurate ab initio data for potential energy curves, and permanent and transition dipole moments, we have obtained the values of the dispersion coefficients between identical polar molecules (LiNa, LiK, LiRb, LiCs, NaK, NaRb, NaCs, KRb, KCs, RbCs) in an arbitrary vibrational level of their electronic ground state. A careful analysis of the importance of the various kinds of transitions contributing to the sum has been performed. The C_6 values significantly decrease with increasing vibrational levels towards the sum of the C_6 coefficients between the four involved atomic pairs. For the lowest vibrational levels the C_6 parameter varies from about 10^4 atomic units for KRb up to 10^7 atomic units for NaCs, which will lead to different collisional regimes at ultracold temperatures.

MO 13.11 Tue 16:30 Poster.IV

High-resolution LIR-spectroscopy of molecular ions — ●OSKAR ASVANY, SANDRA BRÜNKEN, LARS KLUGE, SABRINA GÄRTNER, and STEPHAN SCHLEMMER — I. Physikalisches Institut, Universität zu Köln

Laser Induced Reaction (LIR) is a powerful technique for the spectroscopy of molecular ions as well as the study of state-specific rate coefficients. It is based on trapping mass-selected ions in a cryogenic ion trap and probing their laser-induced excitation by the outcome of an endothermic ion-molecule reaction. In particular, the combination of cold ions with a narrow-bandwidth optical parametric oscillator (OPO) enables highly accurate determination of rovibrational transitions. In this poster, the application of this technique to H_3^+ , CH_2D^+ and CH_5^+ in the 3 micron wavelength region is presented. H_3^+ and CH_2D^+ are molecules of mostly astrophysical interest. For CH_2D^+ , the presented method yielded rovibrational lines known with MHz accuracy. A standard asymmetric rotor model fitted to the data transferred this accuracy to the ground state rotational transitions. The method demonstrated here could be a useful way to determine rotational transitions which are difficult to measure in the microwave region. The ion CH_5^+ is known to be the prototype of a floppy molecule. For this reason, its chaotic spectrum presented by Takeshi Oka in 1999 is still unexplained. Applying the LIR-technique, the prospects of obtaining high-resolution information of CH_5^+ are discussed. In this particular case, cooling of this floppy ion to populate only the lowest states will be crucial for the feasibility of the experiment.

MO 13.12 Tue 16:30 Poster.IV

Ultrafast Circular Dichroism Investigation of the Ring Opening in 7-Dehydrocholesterol — ●JULIA MEYER-ILSE^{1,2}, DENIS AKIMOV², and BENJAMIN DIETZEK^{1,2} — ¹Institute of Physical Chemistry and Abbe Center of Photonics, Friedrich-Schiller University Jena, Jena, Germany — ²Institute of Photonic Technologies (IPHT) Jena e.V., Jena, Germany

UV-femtosecond time-resolved circular dichroism (TRCD) spectroscopy has been used to study the ultrafast changes of chirality in a small molecular biological paradigm sample, 7-dehydrocholesterol (7-DHC). Upon UV-photoexcitation, 7-DHC undergoes a ring opening to produce previtamin D3 and two of the chiral centers of 7-DHC are removed, which impacts the overall chirality of the molecule. Here, measurements of this chirality change connected to the ring opening of 7-DHC with a time-resolution of 280 fs are reported. With this method a previously described discrepancy concerning the photophysics of 7-DHC was clarified. With our set-up the relaxation time of the chirality change was measured to be 1-2 ps, which corresponds to the shortest time-constant in the transient absorption (TA) measurements, allowing us to assign that time-constant to the ring opening.

MO 13.13 Tue 16:30 Poster.IV

Femtosecond Coherence Spectroscopic Study of the Onset of Chemical Denaturation of Myoglobin upon Addition of Minor Amounts of Urea — ●JULIA MEYER-ILSE^{1,2}, DENIS AKIMOV², and BENJAMIN DIETZEK^{1,2} — ¹Institute of Physical Chemistry and Abbe Center of Photonics, Friedrich-Schiller University Jena, Jena, Germany — ²Institute of Photonic Technologies (IPHT) Jena e.V., Jena, Germany

The interaction of urea with myoglobin, as a benchmark system for heme-containing proteins, is studied via femtosecond coherence spectroscopy. The work focuses on the effect of urea on the appearance of low-wavenumber oscillations, which are a measure of the geometrical structure of the heme group and its interaction with the polypeptide chain. Pursuing this approach, structural alterations (i.e. changes in the vibrational dynamics of the heme group) are detected at denaturant concentrations below the full denaturation limit of 6M urea

for myoglobin. In particular, the low-wavenumber oscillation associated with the heme-doming (i.e. the out-of-plane vibration of the porphyrin macrocycle) is found to appear spectrally shifted with a concentration of only 3M urea. These results suggest that the local environment around the heme is already altered despite the fact that macroscopic unfolding as manifested in the thermodynamic properties of the polypeptide chain is not complete at these urea concentrations.

MO 13.14 Tue 16:30 Poster.IV

Investigations on the Circular Dichroism in the Photoelectron Angular Distributions of Camphor and Fenchone using circularly polarized Femtosecond UV-laser pulses — CHRISTIAN LUX, •VANESSA BRANDENSTEIN, TOM BOLZE, CRISTIAN SARPE, MATTHIAS WOLLENHAUPT, and THOMAS BAUMERT — Universität Kassel, Institut für Physik und CINSaT, D-34132 Kassel, Germany

Enantiomers of a chiral molecule that are non super imposable mirror images of each other show almost the same physical properties. In the recent past experiments on enantiomers based on laser irradiation using circularly polarized ultrashort laser pulses [1,2] or synchrotron radiation [3] were realized for chiral molecules.

In this contribution we investigate the effect of Circular Dichroism on the Photoelectron Angular Distributions (PECD) in the Resonance Enhanced Multi-Photon Ionization of Camphor and Fenchone employing femtosecond ultraviolet-laser pulses [4]. Our experiments have been extended to studies of the Above Threshold Ionization and dependencies of the PECD on parameters like intensity, chirp and ellipticity.

[1] C. Logé, A. Bornschlegl, U. Boesl, *Anal. Bioanal. Chem.* **395**, 1631-1639 (2009)

[2] P. Horsch, G. Urbasch, K.-M. Weitzel, *Z. Phys. Chem.* **225**, 587-594 (2011)

[3] I. Powis in S. A. Rice (Ed.): *Adv. Chem. Phys.* **138**, 267-329 (2008)

[4] C. Lux, M. Wollenhaupt, T. Bolze, Q. Liang, C. Sarpe, T. Baumert (*in preparation*) (2011)

MO 13.15 Tue 16:30 Poster.IV

Accessing higher-lying Reaction Pathways of a Molecular Switch by Femtosecond Pump–Repump–Probe Spectroscopy — •STEFAN RUETZEL, MARTIN KULLMANN, JOHANNES BUBACK, PATRICK NUERNBERGER, and TOBIAS BRIXNER — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

Many photochromic compounds and their ultrafast dynamics after photoexcitation have been studied in recent years by means of femtosecond spectroscopy such as transient absorption measurements. However, the role of higher-lying excited states in these photoreactions has not been explored for many of these systems. By exploiting spectrally resolved pump–repump–probe transient absorption spectroscopy we are able to resolve the kinetics that happen after excitation to higher-lying electronic states.

Here we present pump–repump–probe data of the molecular switch 6,8-dinitro-1',3',3'-trimethylspiro[2H-1-benzopyran-2,2'-indoline], a photochromic system present in two ring-open isomers in solution which differ in a cis/trans configuration of a double bond. The pump pulse excites the molecule to its first electronically excited state, the second pulse is resonant with excited-state absorption, and the whitelight probe pulse allows the observation of many possible product absorptions. Our data suggests the formation of new absorbing species triggered by optical repumping of the main isomer. A detailed data analysis as well as a discussion of possible photoproducts to be formed after repumping is presented.

MO 13.16 Tue 16:30 Poster.IV

Fragment momentum distributions obtained from coupled electron-nuclear dynamics — •KILIAN HADER and VOLKER ENGEL — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Emil-Fischer-Str. 42, 97074 Würzburg

We theoretically investigate fragmentation processes induced by femtosecond laser pulses within a model which incorporates electronic and nuclear motion. Single-pulse excitation leads to diffraction patterns in the electron-momentum distribution which depend on the nature of the electronic state and also on the nuclear charge distribution. Additional structures appear in the nuclear-momentum distribution if two time-delayed pulses produce fragments in the same dissociation channel. It is shown that these functions are modified by the electronic degree-of-freedom. A simultaneous excitation of two different electronic state results in further interferences which are related to electronic wave-

packet dynamics on the attosecond time-scale.

MO 13.17 Tue 16:30 Poster.IV

Ionisation von H_2^+ in starken Laserfeldern — •KEVIN PAHL, MAX SCHÜTT, MATTHIAS ODENWELLER, LOTHAR SCHMIDT, MAKSIM KUNITSKI, JIAN WU, JASMIN TITZE, MARKUS WAITZ, DANIEL METZ, CHRISTOPH GOIHL, FLORIAN TRINTER, JÖRG VOIGTSBERGER, CHRISTIAN MÜLLER, TILO HAVERMEIER, HENDRIK SANN, HORST SCHMIDT-BÖCKING und REINHARD DÖRNER — Institut für Kernphysik, Farnkfurt a.M.

Untersuchung der Ionisation von H_2^+ in starken Laserfeldern. Die Moleküle werden durch Stoßionisation ionisiert und in einem Teilchenbeschleuniger beschleunigt. Der Ionenstrahl wird anschließend mit einem Femtosekundenlaser, der Wellenlänge von 400nm, mit einer Leistung von $5 \cdot 10^{14} \text{W/cm}^2$ im Fokus, zum Überlapp gebracht. Dabei können alle bei der Ionisation freiwerdenden Ionen und Elektronen gemessen werden. Durch eine Messung der 2-dimensionalen Ortsprojektion der Reaktionsprodukte und der Flugzeit, kann die Reaktion im 3-dimensionalen Impulsraum vollständig rekonstruiert und analysiert werden. Darüber hinaus ermöglicht dies eine Berechnung der Reaktionsenergien und Darstellung der jeweiligen Winkelverteilung.

MO 13.18 Tue 16:30 Poster.IV

Ionisation von NH_2^+ in starken Laserfeldern — •MAX SCHÜTT, KEVIN PAHL, MATTHIAS ODENWELLER, LOTHAR SCHMIDT, MAKSIM KUNITSKI, JIAN WU, JASMIN TITZE, MARKUS WAITZ, DANIEL METZ, CHRISTOPH GOIHL, FLORIAN TRINTER, JÖRG VOIGTSBERGER, CHRISTIAN MÜLLER, TILO HAVERMEIER, HENDRIK SANN, HORST SCHMIDT-BÖCKING und REINHARD DÖRNER — Goethe-Universität Frankfurt am Main

Untersuchung der Ionisation von NH_2^+ in starken Laserfeldern. Die Moleküle werden durch Stoßionisation ionisiert und in einem Teilchenbeschleuniger beschleunigt. Der Ionenstrahl wird anschließend mit einem Femtosekundenlaser mit einer Leistung $5 \cdot 10^{14} \text{W/cm}^2$ im Fokus und einer Wellenlänge von 400nm, zum Überlapp gebracht. Dabei können alle bei der Ionisation freiwerdenden Ionen und Elektronen gemessen werden. Durch eine Erfassung der 2-dimensionalen Ortsprojektion der Reaktionsprodukte und der Flugzeit, kann die Reaktion im 3-dimensionalen Impulsraum vollständig rekonstruiert und analysiert werden. Darüber hinaus ermöglicht dies eine Berechnung der Reaktionsenergien und Darstellung der jeweiligen Winkelverteilung.

MO 13.19 Tue 16:30 Poster.IV

Controlling large molecules at kHz repetition rates — SEBASTIAN TRIPPEL¹, TERENCE G. MULLINS¹, •NELE MÜLLER¹, KAROL DLUGOLECKI¹, and JOCHEN KÜPPER^{1,2} — ¹Center for Free-Electron Laser Science, DESY, Hamburg — ²University of Hamburg

With our new experimental setup we aim for studying ultrafast dynamics of large and complex molecules directly in the molecular frame. In first benchmark experiments we create supersonic, cold beams of prototypical iodobenzene (C_6H_5I) molecules at high repetition rates – up to 1 kHz. These molecular beams are quantum-state selected by dc electric fields [1,2] and, subsequently, laser aligned and mixed-field oriented by strong picosecond laser fields and weak dc electric fields [2]. The resulting strongly aligned and oriented molecular samples are characterized by strong-field ionization using femtosecond laser pulses and velocity-map imaging of the produced ions to derive the angular distribution of the molecules. The degrees of alignment and orientation are characterized as a function of repetition rate, state selection, and laser parameters. In the future, the high repetition rate will allow us to investigate weak processes in molecular dynamics, exploiting, for instance, molecular-frame photoelectron angular distributions [3].

[1] F. Filsinger et al., *Angew. Chem. Int. Ed.*, **48**, 6900-6902 (2009)

[2] L. Holmegaard et al., *Phys. Rev. Lett.*, **102**, 023001 (2009)

[3] L. Holmegaard et al., *Nature Physics*, **6**, 428 (2010)

MO 13.20 Tue 16:30 Poster.IV

Femtosecond Time-Resolved Transient Grating Spectroscopy for the Investigation of Exciton Dynamics in Thin Films of PTCDA — •TAHIR ZEB KHAN, KHADGA J. KARKI, MAHESH NAMBOODIRI, and ARNULF MATERNY — Research Center for Functional Materials and Nanomolecular Science, Jacobs University, Campus Ring 1, D-28759 Bremen, Germany

Elementary processes like energy transfer, charge transport, and exciton diffusion in thin films occur on time scales of femtoseconds. Time-resolved photo-electron spectroscopy, a technique limited to special-

ized ultra-high vacuum environment and the proper choice of substrate, has been used to study ultrafast processes in sub-nanometer thin films so far. In our contribution, we show that a transient (population) grating created by the interference of femtosecond laser pulses can be applied successfully to access ultrafast processes in such films under ambient conditions. Our investigations of exciton dynamics in 1.4 ± 0.2 and 0.4 ± 0.2 nm thin films, formed by nano crystals of 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) on glass and mica, show that the dynamics differ with the crystal size, possibly due to the confinement-induced changes in the electronic structure. The technique is sensitive enough to investigate the dynamics in systems, where only 20% of the surface is covered by nano crystals. This is an important prerequisite for studying ultrafast dynamics on surfaces, interfaces, functionalized materials, organic semiconductors, and quantum phenomena in ordered structures of reduced dimensions, such as quantum dots and graphene sheets.

MO 13.21 Tue 16:30 Poster.IV

Photoinduced Processes in a Low-Spin Cobalt(II) Semiquinonate Complex — ●FABIAN RUPP¹, KATHARINA CHEVALIER¹, MATTHIAS M.N. WOLF¹, MICHELE GRAF², HARALD KELM², HANS-JÖRG KRÜGER², and ROLF DILLER¹ — ¹Dept. of Physics, Univ. Kaiserslautern — ²Dept. of Chemistry, Univ. Kaiserslautern, 67663 Kaiserslautern, Germany

Metal complexes undergoing valence tautomerism and spin-crossover by external stimuli may be utilized as novel molecular switches [1]. Here we study ultrafast photoinduced processes in the first cobalt(II) semiquinonate complex, that displays spin-crossover properties rather than valence tautomerism [2], by means of femtosecond time-resolved pump-probe-spectroscopy in solution. After photoexcitation of $[\text{Co}(\text{L-N}_4\text{tBu}_2)(\text{dbsq})](\text{B}(p\text{-C}_6\text{H}_4\text{Cl})_4)$ we probe in the visible/near-infrared (IR) and mid-IR range for dynamical and structural information on the transient species [3]. The observed kinetics support the parallel formation of two cobalt(III) catecholate species with different spin multiplicity that replenish the ground state on a picosecond time scale. The model will be advanced by quantum chemical calculations and further time-resolved as well as steady-state studies of similar complexes that may allow to indentify vibrational marker bands for the assignment of possible redox- and spin-states.

[1] J.-F. Letard et al., *Top. Curr. Chem.* **235**, 221 (2004)

[2] M. Graf et al., *Angew. Chem., Int. Ed.* **49**, 950 (2010)

[3] M.M.N. Wolf et al., *Phys. Chem. Chem. Phys.* **10**, 4264 (2008)

MO 13.22 Tue 16:30 Poster.IV

Efficient and robust strong-field control of population transfer in sensitizer dyes with designed femtosecond laser pulses — JOHANNES SCHNEIDER, MATTHIAS WOLLENHAUPT, ANDREAS WINZENBURG, ●TOBIAS BLUMENSTEIN, TIM BAYER, JENS KÖHLER, RÜDIGER FAUST, and THOMAS BAUMERT — University of Kassel, Institute of Physics and CINSaT, D-34132 Kassel, Germany

We demonstrate control of electronic population transfer in molecules with the help of shaped femtosecond laser pulses. To that end we investigate two photosensitizer dyes in solution being prepared in the triplet ground state. Excitation within the triplet system is followed by intersystem crossing and the corresponding singlet fluorescence is monitored as a measure of population transfer in the triplet system. We record control landscapes with respect to the fluorescence intensity on both dyes by a systematic variation of laser pulse shapes combining second order and third order dispersion. In the strong-field regime we find highly structured topologies with large areas of maximum or minimum population transfer being robust with respect to the applied laser intensities. We then compare our experimental results with simulations on generic molecular potentials by solving the TDSE for excitation with shaped pulses. The analysis of the regions of maximum or minimum population transfer reveals that coherent processes control the outcome of the excitation process. Within this context we give an outlook on the application of strong field controlled fluorescence to nonlinear microscopy.

MO 13.23 Tue 16:30 Poster.IV

Investigation of vibrational coherence generation by femtosecond two-pulse excitation experiments — ●JAN PHILIP KRAACK, MARCUS MOTZKUS, and TIAGO BUCKUP — Physikalisches-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, D-69120 Heidelberg, Germany

Vibrational coherences in nonlinear optical spectroscopy are prepared by two distinct light-matter interactions. These may take place within

the temporal envelope of a single excitation pulse of femtosecond time duration in, e.g., two-pulse pump-probe spectroscopy. Alternatively, each interaction may take place within the temporal envelope of independent excitation pulses as in, e.g., three-pulse Degenerate Four-Wave-Mixing (DFWM)[1]. The application of two distinct excitation pulses in DFWM offers important advantages over single excitation pulse techniques regarding investigations of electronic coherence dynamics. We experimentally and theoretically investigated effects of variable interpulse delays between excitation pulses in spectrally-resolved and -integrated DFWM. Clear oscillatory modulation of normal mode signal intensities is observed for a series of samples with different vibrational characteristics when the interpulse delay is scanned. These modulation effects are strongly dependent on the displacements between involved electronic states as well as the number of involved vibrational modes.

[1]Kraack, J. P.; Motzkus, M.; Buckup, T. *The Journal of Chemical Physics* 2011, 135, 224505.

MO 13.24 Tue 16:30 Poster.IV

CRASY: Correlated Rotational Alignment Spectroscopy of Molecules and Clusters — CHRISTIAN SCHRÖTER and ●THOMAS SCHULTZ — Max-Born-Institut, Berlin

When a molecule is ionized, the formed electron and ion can be detected with quantum yields close to one, leading to an extraordinarily sensitive characterization of molecular mass and electronic structure. By using pump-probe ionization schemes, the characterization can be extended to photoexcited species to observe photochemical reactions in real time. The information content of such experiments, however, is insufficient for spectroscopic assignment of molecular structure in all but the most trivial molecules.

Rotational spectroscopy is a very sensitive tool to characterize molecular structure. We recently demonstrated the correlated measurement of rotational spectra and pump-probe ionization spectra by correlated rotational alignment spectroscopy (SCIENCE 333, 1011 (2011)). The experiment combines the extraordinary sensitivity of ionization spectroscopy with the high-resolution information of rotational spectroscopy. Through the simultaneous determination of molecular masses, electron binding energies, and rotational structure for multiple species in a sample, CRASY can generate spectroscopic data of a new quality and with unprecedented information content. Our poster will present the experimental technique and show recent results of CRASY measurements.

MO 13.25 Tue 16:30 Poster.IV

High Harmonic Spectroscopy of NO₂: Electronic Dynamics and Molecular Dissociation — ●CHUNG-HSIN YANG¹, CHRISTIAN NEIDEL¹, JESSE KLEI¹, ARJAN GJUSBERTSEN³, MARC VRAKING¹, and HANS JAKOB WÖRNER² — ¹Max-Born-Institut, Berlin — ²ETH, Zürich — ³AMOLF, Amsterdam

Time-resolved photoelectron and photoion velocity map imaging (VMI) experiments have been used to study NO₂ excited close to its first dissociation limit, leading to NO (XII) and O (3P) fragments. The NO₂ molecule was excited to its A ²B₂ excited electronic state by one pump photon at a center wavelength of 395 nm, followed by a probe laser pulse in the XUV wavelength region from a high-harmonics source. The first excited electronic state of NO₂, A ²B₂, is embedded within the X ²A₁ electronic ground state and is strongly coupled to the X ²A₁ state via a conical intersection between the two potential energy surfaces. By varying the time delay between the pump and probe lasers, we probe the photodynamics of NO₂ by measuring photoion and photoelectron momentum distributions. In our measurements, both NO⁺ and O⁺ yields show exponential growth (1-1.5ps rise time) corresponding to the dissociation time scale observed from previous energy dependence studies. For the photoelectron results, some channels with hundred femtoseconds or picoseconds dynamics have been ascribed to the ionization of NO₂ molecule in X ²A₁ or A ²B₂ state, or fragments. However, contributions from electrons correlating with different ions and produced by different high harmonics result in a large complexity of photoelectron images.

MO 13.26 Tue 16:30 Poster.IV

Time-resolved photoelectron imaging of excited state dynamics in nitric oxide (NO) in the VUV range — PETER TRABS, FRANZISKA BUCHNER, ●ANDREA LÜBCKE, ARNAUD ROUZÉE, HANS-HERMANN RITZE, MASOOD GHOTBI, and MARC VRAKING — Max-Born Institut Berlin

40 fs tuneable VUV pulses in the range of 147 nm - 150 nm are used

to trigger electron dynamics in Rydberg states of NO. A second delayed pulse at 800 nm probes the excited state by photoionization. A velocity map imaging spectrometer is used to measure the angular and kinetic energy distribution of the ejected photoelectrons in dependence of the delay between pump and probe pulses. We observe three photoelectron lines and find different oscillations in the photoelectron yield, the kinetic energy and the angular distribution. These results are interpreted in terms of beating between different vibronic states.

MO 13.27 Tue 16:30 Poster.IV

The test of approximate relation between inter-nuclear distances and vibration frequencies in a few-atomic molecule — ●VLADIMIR DAMLJANOVIC — Institute of Physics Belgrade, Pregrevica 118, 11080 Belgrade, Serbia

Recently, the author has found a group of coordinate transformations that are symmetries of the electronic effective potential and the potential seen by nuclei in a molecule subjected to no external fields [arXiv:1111.4788v1]. In the lowest order approximation for the electronic effective potential adapted to these symmetries, one obtains the approximate relation between the equilibrium distances among nuclei in the molecule and its vibration frequencies. In this contribution we have tested this approximation for a variety of simple molecules.

MO 13.28 Tue 16:30 Poster.IV

Multidimensional Quantum Dynamics of Coupled Carbonyl Vibrations — ●MATEUSZ LISAJ and OLIVER KÜHN — Institute of Physics, Rostock University, Rostock, Germany

The six coupled carbonyl vibrations in the model system $Fe_2(\mu SC_3H_6 - S)(CO_6)$ are investigated. First, quantum chemical (DFT) calculations are performed to span a six-dimensional potential energy surface (PES) in terms of normal mode coordinates. Relevant anharmonic couplings are identified and strategies for representation of PES and dipole moment surface are derived. The quantum dynamics of this model system is studied on the basis of the Multiconfiguration time-dependent Hartree method. Emphasis is put on the signatures of anharmonic couplings in linear and nonlinear infrared spectroscopy.

MO 13.29 Tue 16:30 Poster.IV

Ultrafast Exciton Quenching upon Geometry Deformation in Molecular Aggregates — ●ALEXANDER SCHUBERT¹, VOLKER SETTELS¹, WEN-LAN LIU^{1,2}, FRANK WÜRTHNER¹, CHRISTOPH MEIER³, REINHOLD FINK^{1,4}, STEFAN SCHINDLBECK⁵, STEFAN LOCHBRUNNER⁶, BERND ENGELS¹, and VOLKER ENGEL¹ — ¹Universität Würzburg — ²Universität Heidelberg — ³Université de Toulouse — ⁴Universität Tübingen — ⁵LMU München — ⁶Universität Rostock

The efficiency of energy transport in molecular pi-aggregates is strongly attenuated by de-excitation mechanisms. We investigated experimentally and theoretically dimer aggregates of 3,4,9,10-perylene tetracarboxylic bisimide acid, exemplarily.

The measured absorption spectra could be interpreted assuming dipole-dipole coupling and a single effective vibrational monomer mode. An additional intermolecular torsional mode explained the fluorescence spectroscopic measurements indicating a long radiative lifetime and a low fluorescence yield. We now established an insight into

the decay dynamics of optically excited state and the reaction path to the fluorescing state. Transient absorption measurements show that the excited state decays non-radiatively on an ultrafast fs-time-scale. This decay can be reproduced by a geometry change which increases the non-adiabatic transition effectivity. For that purpose we determined potential energy curves along a reaction coordinate relating the Franck-Condon geometry to a charge transfer configuration where the monomers exhibit the anion and cation geometry.

MO 13.30 Tue 16:30 Poster.IV

Non-adiabatic on-the-fly molecular dynamics on the formation of the DNA Dewar photolesion: Implementation of ONIOM and CASPT2 — ●SVEN OESTERLING, ARTUR NENOV, BENJAMIN P. FINGERHUT, and REGINA DE VIVIE-RIEDLE — Ludwig Maximilians Universität München, Department Chemie

Semiclassical on-the-fly dynamics provide a way to simulate molecular processes of moderate sized systems. Treating the nuclei classically, abolishes the need to precompute potential energy surfaces, and thus allows for a full dimensional treatment of the molecular degrees of freedom. The electronic properties are computed with quantum chemical methods, adequate for system-size and nature of the problem. This combination makes the whole approach an useful tool to investigate non-adiabatic reactions in many biologically relevant molecules, such as the nucleobases.

In the process of describing the formation and reversion of the DNA Dewar photolesion, we implemented an interface for the Molpro quantum chemistry package, in the Newton-X dynamics package. The two main features are the complete active space perturbation theory (CASPT2) and a hierarchical layer scheme (ONIOM). While CASPT2 yields very precise results for the electronically excited bases, the ONIOM method enables embedding the photoactive fragments into the phosphate-desoxyribose backbone, treated with computationally less demanding ground-state methods. In this way both, photochemical, as well as sterical effects can be accounted for, in an appropriate fashion.

MO 13.31 Tue 16:30 Poster.IV

Rotational effects on enantioseparation — ●ANDREAS JACOB and KLAUS HORNBERGER — Universität Duisburg-Essen, Fakultät für Physik, Lotharstraße 1-21, 47057 Duisburg

Recently, several ideas to separate enantiomers have been proposed, i.e. to split molecules in a left handed configuration from their right handed mirror state [1,2]. They are based on the dynamics caused by the equations of motion in an adiabatic basis produced by laser induced gauge potentials. Since the effect of molecular rotation has been neglected in these studies, we study the influence of the orientation state on the enantioseparation by numerical integration of the full molecular rotation state. We find that the potential from the adiabatic dressed state approach cannot be recovered, even in the rotational ground state. The obtained time-averaged interaction potentials and the associated forces are then strongly diminished, but they can still exhibit chiral sensitivity.

[1] Li, Bruder and Sun, Physical Review Letters 99, 130403 (2007)

[2] Li and Shapiro, The Journal of Chemical Physics 132, 194315 (2010)