

Molecular Physics Division Fachverband Molekülphysik (MO)

Gereon Niedner-Schatteburg
Fachbereich Chemie
Technische Universität Kaiserslautern
Erwin-Schrödinger-Straße
67663 Kaiserslautern
gns@chemie.uni-kl.de

Overview of Invited Talks and Sessions

(Lecture rooms: PH/HS1 and PH/SR106; Poster: C/Foyer)

Invited Talks

MO 2.1	Mon	11:30–12:00	PH/HS1	Simulating the control of molecular reactions via modulated light fields: From gas phase to solution — ●REGINA DE VIVIE-RIEDLE
MO 3.1	Mon	14:30–15:00	PH/HS1	Vibrational coherence in excited electronic states studied with multidimensional time-resolved spectroscopy — TIAGO BUCKUP, ●MARCUS MOTZKUS
MO 8.1	Tue	11:00–11:30	PH/HS1	Novel computational approaches to molecular electronic-structure theory — ●WIM KLOPPER
MO 9.1	Tue	14:30–15:00	PH/HS1	Control and Spectroscopy of Chiral Systems in the Condensed Phase — ●TOBIAS BRIXNER
MO 12.1	Wed	11:00–11:30	PH/HS1	Generating high-valent iron with light. Photochemical dynamics — ●PETER VÖHRINGER
MO 13.1	Wed	11:00–11:30	PH/SR106	Cryo-stored ion beams for studying neutral production in molecular fragmentation — ●ANDREAS WOLF
MO 15.1	Wed	14:30–15:00	PH/SR106	Vibrational Spectroscopy of Cluster Complexes with Free Electron Lasers: Surface Science en Miniature — ●ANDRÉ FIELICKE
MO 17.1	Thu	11:00–11:30	PH/HS1	State-selective attachment of helium atoms to stored, cold molecular ions — ●SANDRA BRÜNKEN, LARS KLUGE, ALEXANDER STOFFELS, OSKAR ASVANY, STEPHAN SCHLEMMER
MO 18.1	Thu	11:00–11:30	PH/SR106	cis-trans Isomerization, Ion-Pumps and pH-Sensor: From Molecular Interactions to Biological Function — ●ROLF DILLER, PATRICK SINGER, MIRIAM COLINDRES, PHILIPP ALT, EKKEHARD NEUHAUS, TILMAN LAMPARTER
MO 19.1	Thu	14:30–15:00	PH/HS1	Luminescence properties of mass-selected lanthanoid complexes: a study involving gas-phase ion trapping, ion deposition into neon matrices, and computations. — ●JEAN-FRANCOIS GREISCH, BASTIAN KERN, MICHAEL E. HARDING, JIŘÍ CHMELA, BERNHARD SCHÄFER, ARTUR BÖTTCHER, WIM KLOPPER, MARIO RUBEN, DETLEF SCHOOSS, DMITRY STRELNIKOV, PATRICK WEIS, MANFRED M. KAPPES
MO 20.1	Thu	14:30–15:00	PH/SR106	Controlling charge migration in molecules — ●ALEXANDER I. KULEFF

Invited talks of the joint symposium SYDM

See SYDM for the full program of the symposium.

SYDM 1.1	Tue	11:00–11:40	C/gHS	Searching for New Physics Effects in the Muon g -Factor — ●B. LEE ROBERTS
SYDM 1.2	Tue	11:40–12:20	C/gHS	Dedicated storage ring EDM methods — ●YANNIS SEMERTZIDIS
SYDM 2.1	Tue	14:30–15:10	C/gHS	The experimental search for the neutron electric dipole moment — ●KLAUS KIRCH
SYDM 2.2	Tue	15:10–15:50	C/gHS	The muon g-2: where we are, what does it tell us? — ●FRIEDRICH JEGERLEHNER

Invited talks of the joint symposium SYPS

See SYPS for the full program of the symposium.

SYPS 1.1	Tue	17:00–17:30	K/HS1	Feshbach resonances and the production of ultracold molecules — •JEREMY M. HUTSON
SYPS 1.2	Tue	17:30–18:00	K/HS1	New frontiers in quantum simulation with ultra-cold polar molecules — •ANA MARIA REY
SYPS 1.3	Tue	18:15–18:45	K/HS1	Ground-state molecules near quantum degeneracy: the nuts and bolts — •HANNES-CHRISTOPH NÄGERL
SYPS 1.4	Tue	18:45–19:15	K/HS1	Prospects and future directions with quantum gases of ultracold polar molecules — •SILKE OSPELKAUS

Invited talks of the joint symposium SYNG

See SYNG for the full program of the symposium.

SYNG 1.1	Thu	11:00–11:30	C/gHS	Development of a new facility for measuring 81Kr and 85Kr at ultra-trace level in environmental samples. — •BERNARD LAVIELLE, ERIC GILABERT, BERTRAND THOMAS, ROMAIN REBEIX, GRÉGORIE CANCHEL, CHRISTOPHE MOULIN, SYLVAIN TOPIN, FABIEN POINTURIER
SYNG 1.2	Thu	11:30–12:00	C/gHS	Atom counting system to measure trace krypton contamination in ultra-pure xenon — •ANDRE LOOSE, TANYA ZELEVINSKY, ELENA APRILE
SYNG 1.3	Thu	12:00–12:30	C/gHS	Krypton-85 and Radioxenon: Environmental Tracers and Indicators for Nuclear Activities — •CLEMENS SCHLOSSER, VERENA HEIDMANN, MARTINA KONRAD, SABINE SCHMID
SYNG 2.1	Thu	14:30–15:00	C/gHS	Using Noble Gases to Understand the History of Terrestrial Volatiles — •DON PORCELLI
SYNG 2.2	Thu	15:00–15:30	C/gHS	Noble gas analysis in water: from temperature reconstruction over excess formation to oxygen turnover on environmentally relevant time scales — •ROLF KIPFER, MATTHIAS BRENNWALD
SYNG 2.3	Thu	15:30–16:00	C/gHS	Applications of Noble Gases in Oceanography — •PETER SCHLOSSER, ROBERT NEWTON, GISELA WINCKLER, ANGELICA PASQUALINI

Sessions

MO 1.1–1.6	Mon	11:30–13:15	M/HS1	Atomic clusters (with MO)
MO 2.1–2.5	Mon	11:30–13:00	PH/HS1	Quantum Control
MO 3.1–3.7	Mon	14:30–16:30	PH/HS1	Femtosecond Spectroscopy 1
MO 4.1–4.8	Mon	14:30–16:30	PH/SR106	Cold Molecules 1
MO 5.1–5.23	Mon	17:00–19:00	C/Foyer	Posters 1: Novelties in Molecular Physics
MO 6.1–6.8	Mon	17:00–19:00	C/Foyer	Atomic clusters (with MO)
MO 7.1–7.7	Tue	11:00–13:00	PH/HS2	Ion Traps, Molecules, Clusters, Decay and Reactions
MO 8.1–8.7	Tue	11:00–13:00	PH/HS1	Theory: Quantum Chemistry
MO 9.1–9.7	Tue	14:30–16:30	PH/HS1	Femtosecond Spectroscopy 2
MO 10.1–10.7	Tue	14:30–16:15	PH/SR106	Experimental Techniques
MO 11.1–11.23	Tue	17:00–19:00	C/Foyer	Posters 2: Novelties in Molecular Physics
MO 12.1–12.6	Wed	11:00–12:45	PH/HS1	Photochemistry and Catalysis
MO 13.1–13.7	Wed	11:00–13:00	PH/SR106	Collisions & Energy Transfer
MO 14.1–14.7	Wed	14:30–16:30	PH/HS1	Cold Molecules 2
MO 15.1–15.7	Wed	14:30–16:30	PH/SR106	Clusters in Molecular Physics (with A & MS)
MO 16.1–16.23	Wed	17:00–19:00	C/Foyer	Posters 3: Novelties in Molecular Physics
MO 17.1–17.7	Thu	11:00–13:00	PH/HS1	Cold Molecules 3
MO 18.1–18.7	Thu	11:00–13:00	PH/SR106	Biomolecules
MO 19.1–19.6	Thu	14:30–16:15	PH/HS1	Electronic Spectroscopy
MO 20.1–20.8	Thu	14:30–16:45	PH/SR106	Theory: Molecular Dynamics
MO 21.1–21.22	Thu	17:00–19:00	C/Foyer	Posters 4: Novelties in Molecular Physics
MO 22.1–22.8	Fri	11:00–13:00	PH/HS1	Femtosecond Spectroscopy 3
MO 23.1–23.7	Fri	11:00–12:45	PH/SR106	Progress on Various Topics in Molecular Physics

Annual General Meeting of the Molecular Physics Division

Mittwoch 13:00–13:30 PH/SR106

- Bericht des Sprechers
- Vorschläge für Symposien (Hannover 2016)
- Vorschläge für Plenarsprecher (Hannover 2016)
- Verschiedenes

MO 1: Atomic clusters (with MO)

Time: Monday 11:30–13:15

Location: M/HS1

Invited Talk

MO 1.1 Mon 11:30 M/HS1

Dynamic x-ray imaging of clusters in strong fields — ●THOMAS FENNEL — University of Rostock, 18051, Rostock, Germany

Intense laser-cluster interactions allow the fundamental investigation of collective and correlated processes in nanoscale plasmas, including ionization avalanching, plasmon-assisted electron acceleration, attosecond plasma wave dynamics, and plasma expansion. With the rapidly developing capabilities of FELs, novel routes to the direct time-resolved imaging of the underlying dynamics are emerging [1]. I will discuss the feasibility of pump - probe scattering experiments for tracing cluster dynamics via diffractive imaging with (sub?)femtosecond resolution. The recently developed microscopic particle-in-cell approach (MicPIC) accounts simultaneously for both the correlated (classical) atomic scale plasma dynamics and electromagnetic wave propagation [2]. Complete MicPIC simulations of NIR pump - x-ray probe experiments on Hydrogen clusters are used to (i) identify relevant signatures in the scattering images and to (ii) benchmark a simplified reconstruction scheme to retrieve the (ultra)fast evolution of the cluster density profile [3]. The results suggest the potential to illuminate the dynamics of laser ablation and anisotropic plasma expansion with unprecedented detail. An outlook on routes to attosecond-resolved diffractive imaging and sub-cycle photonic streaking via inelastic x-ray scattering will be given.

[1] I. Barke *et al.*, Nat. Commun. (accepted)[2] C. Varin *et al.*, Phys. Rev. Lett. **108**, 175007 (2012)[3] C. Peltz *et al.*, Phys. Rev. Lett **113**, 133401 (2014)

MO 1.2 Mon 12:00 M/HS1

Experimental determination of absolute cross sections for cluster-specific decay mechanisms — ●ANDREAS HANS¹, ANDRÉ KNIE¹, MARKO FÖRSTEL², PHILIPP SCHMIDT¹, UWE HERGENHAHN², and ARNO EHRESMANN¹ — ¹Institut für Physik, Universität Kassel, Heinrich-Plett-Straße 40, 34132 Kassel — ²Max-Planck-Institut für Plasmaphysik, c/o HZB-Bessy II, Albert-Einstein-Straße 15, 12489 Berlin

The knowledge of absolute values for cross sections of specific processes is of high interest in many fields of physics and especially for applications. In atomic clusters, decay mechanisms can differ significantly from those dominant in atoms. Absolute cross sections of these processes are attractive in many contexts, e.g. in astrophysics or applications of interatomic Coulombic decay (ICD). We present a new method to determine absolute cross sections for cluster-specific decay mechanisms using photon-induced fluorescence spectroscopy of a partially condensed gas jet. Once calibrated, this method also allows the characterization of cluster jets. In a first experiment, absolute cross sections of resonant ICD in Ne clusters and photon emission after inner-valence excitation in Ar clusters were measured.

MO 1.3 Mon 12:15 M/HS1

Investigation of resonant interatomic coulombic decay in neon clusters by dispersed fluorescence spectroscopy — ●LTAIEF BEN LTAIEF¹, ANDREAS HANS¹, PHILIPP SCHMIDT¹, PHILIPP REISS¹, MARKO FÖRSTEL², UWE HERGENHAHN², TILL JAHNKE³, REINHARD DÖRNER³, ANDRÉ KNIE¹, and ARNO EHRESMANN¹ — ¹Universität Kassel, Heinrich-Plett Straß 40, D-34132 Kassel, Germany — ²Max-Planck- Institut für Plasmaphysik, EURATOM Association, Wendelsteinstr. 1, 17491 Greifswald, Germany — ³Institut für Kernphysik Goethe- Universität Max-von-Laue-Str.1 60438 Frankfurt am Main, Germany

Interatomic Coulombic Decay (ICD) in weakly bound systems, e.g. van-der-Waals clusters or hydrogen bonded clusters, has recently attracted much interest as an efficient and ultrafast process by which the excess energy of electronically excited atoms or molecules is transferred to a neighboring site, thereby, ionizing it. Since its discovery ICD is considered to be a relevant process in radiation chemistry and living tissues by producing low kinetic energy electrons and radical cations which may induce irreparable damage to DNA. So far, most of experiments aiming at ICD-processes used charged particles as probe of the process. Recently we have successfully demonstrated a first unambiguous proof of ICD by undispersed measurements of the emitted photons from neon clusters [1]. Here we report the use of dispersed-fluorescence spectrometry to investigate ICD after resonant excitation in neon clusters.

[1] Knie, A. *et al.* New. J. Phys. **16** 102002 (2014)

MO 1.4 Mon 12:30 M/HS1

Tracing efficient autoionization processes in nanoplasmas — ●BERND SCHÜTTE^{1,2}, MATHIAS ARBEITER³, THOMAS FENNEL³, GHAZAL JABBARI⁴, KIRILL GOKHBERG⁴, ALEXANDER I. KULEFF⁴, JAN LAHL⁵, TIM OELZE⁵, MARIA KRIKUNOVA⁵, MARC J. J. VRAKKING¹, and ARNAUD ROUZÉE¹ — ¹Max-Born-Institut, Berlin, Germany — ²Imperial College London, United Kingdom — ³Universität Rostock, Germany — ⁴Universität Heidelberg, Germany — ⁵Technische Universität Berlin, Germany

Nanoplasmas are generated during the interaction of clusters and large molecules with intense laser pulses from the NIR to the X-ray regime. It was shown that electron-ion recombination leads to a substantial excited state population in nanoplasmas. At sufficiently high laser intensities, multiply-excited atoms and ions can be formed and decay via autoionization. Here we demonstrate an efficient autoionization process in molecular oxygen and atomic clusters interacting with intense NIR pulses. In the case of oxygen clusters, superexcited atoms are formed during the cluster expansion that decay on a time scale of 1 ns. THz streaking reveals that a substantial portion of the electron emission is delayed, which is explained by autoionization processes on (sub-)ps to ns scales. Furthermore, we show that singly-excited Rydberg atoms decay by transferring the excess energy to an electron or to a second Rydberg atom in the environment that gets ionized, similar to interatomic Coulombic decay. The results demonstrate that autoionization processes are crucial for the understanding of nanoplasma dynamics and may strongly influence ion charge state distributions.

MO 1.5 Mon 12:45 M/HS1

Laser-induced delayed electron emission of Co₄⁻ anions — ●CHRISTIAN BREITENFELDT^{1,2}, KLAUS BLAUM², SEBASTIAN GEORGE², JÜRGEN GÖCK², JONAS KARTHEIN², THOMAS KOLLING³, CHRISTIAN MEYER², JENNIFER MOHRBACH³, GERON NIEDNER-SCHATTEBURG³, LUTZ SCHWEIKHARD¹, and ANDREAS WOLF² — ¹Institut für Physik, Ernst-Moritz-Arndt Universität, Felix-Hausdorff-Str. 6, 17487 Greifswald, Germany — ²Max-Planck-Institut für Kernphysik, Saupfercheckweg 1, 69117 Heidelberg, Germany — ³Fachbereich Chemie, Universität Kaiserslautern, Germany

The Cryogenic Trap for Fast ion beams CTF located at the Max-Planck-Institut für Kernphysik is an electrostatic ion beam trap (EIBT) setup. It is well suited to investigate dynamical processes of stored ion beams. Vibrational electron autodetachment (also called delayed electron detachment) is followed by monitoring the rate of neutral particles escaping from the EIBT either as a function of storage time or, in case of laser-induced electron loss processes as a function of the time after laser excitation. Two different ion sources were used: First, a cesium ion sputter source, producing ions with vibrational temperatures up to several hundred Kelvin, second, a laser vaporization source with helium expansion to produce Co₄⁻ anions where the vibrational excitation levels correspond to cryogenic temperatures. The ions were stored in the CTF and the cooling and heating of the ions was probed by the change in the delayed electron detachment rate. The photo excitation measurements were performed as a function of storage time and wavelengths of the laser. Recent results are presented and discussed.

MO 1.6 Mon 13:00 M/HS1

Wide angle X-ray scattering of silica nanoparticles — ●BURKHARD LANGER¹, CHRISTIAN GORONCY¹, CHRISTOPHER RASCHPICHLER¹, FELIX GERKE¹, TORALF LISCHKE², BERNHARD WASSERMANN¹, CHRISTINA GRAF¹, and ECKART RÜHL¹ — ¹Physikalische Chemie, Freie Universität Berlin — ²Max-Planck-Institut für Mikrostrukturphysik, Halle

Amorphous silica nanoparticles are widely used as model systems in materials and life sciences as well as in industrial and pharmaceutical applications. The structure of these particles consists of an amorphous network of SiO₂ containing pores in the nanometer range (1-10 nm). Chemically synthesized silica nanoparticles with a diameter between 150 and 350 nm which are prepared with porous layers are focused with an aerodynamical lens into the interaction region with synchrotron radiation from BESSY II. The experiments were performed in the energy

range of the Si $2p$ regime ($E \approx 100$ eV), where the photon wavelength is comparable to the pore sizes. Deviations in the angle dependent scattering intensity compared to calculations obtained by pure Mie theory for spherical particles are attributed to Rayleigh scattering at the pores

of the nanoparticles. Calculations using Discrete Dipole Approximation Scattering Theory (DDSCAT) and a modified Mie algorithm, both using realistic pore sizes and size distributions, are successfully applied to describe the wide angle X-ray scattering intensities.

MO 2: Quantum Control

Time: Monday 11:30–13:00

Location: PH/HS1

Invited Talk

MO 2.1 Mon 11:30 PH/HS1

Simulating the control of molecular reactions via modulated light fields: From gas phase to solution — ●REGINA DE VIVIE-RIEDLE — LMU München

Optimal control theory and optimal control experiments are state-of-the-art tools to control quantum systems. Both methods have been demonstrated successfully for numerous applications in molecular physics, chemistry and biology. Modulated light pulses could be realized, driving these various control processes. The accessibility of few femtosecond or even attosecond pulses opens the door further to direct observation and steering of electron dynamics. Next to the control efficiency, a key issue is the understanding of the control mechanism. An obvious way is to seek support from theory. In this contribution theoretical studies will be presented that highlight control events ranging from chemical reactions via the steering of nuclear and electronic wavepackets [1,2,3] over directional control of bond breaking in symmetric molecules [4] to control scenarios in solution.

[1] P. von den Hoff, S. Thallmair, M. Kowalewski, R. Siemering, and R. de Vivie-Riedle, *Phys. Chem. Chem. Phys.* 14 (2012), 14460-14485.

[2] M. Kling, P. von den Hoff, I. Znakovskaya, and R. de Vivie-Riedle, *Phys. Chem. Chem. Phys.* 15 (2013), 9448-9467.

[3] S. Thallmair, R. Siemering, P. Kölle, M. Kling, M. Wollenhaupt, T. Baumert, and R. de Vivie-Riedle, in: *Molecular quantum dynamics - from theory to applications*, F. Gatti (Ed.), Springer, 2014, 213-248.

[4] A. S. Alnaser, et al. *Nat. Commun.* 5, article number: 3800 (2014).

MO 2.2 Mon 12:00 PH/HS1

Combination of Chirped and Multipulse Excitation: Control of Population and Vibrational Coherence — ●ELISABETH BRÜHL¹, IDUABO JOHN AFA², CARLES SERRAT², TIAGO BUCKUP¹, and MARCUS MOTZKUS¹ — ¹Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, D-69120 Heidelberg, Germany — ²Universitat Politècnica de Catalunya, Departament de Física i Enginyeria Nuclear, Colom 11, 08222 Terrassa, Spain

Tailoring molecular vibrations is a potential control knob to steer photochemical reactions. Electronic near-resonant excitation with multipulses has been shown to enhance vibrational coherence in the excited state [1]. Additionally, vibrational coherence of the ground state can be also manipulated by using chirped pump pulses via intrapulse impulsive Raman scattering [2]. These two methods of mode selective control with tailored pump beams are now combined to tailor vibrational coherence and population in the electronic excited as well as in the ground state. This is demonstrated by systematic phase shaping of the excitation pulse in transient absorption of dye molecules. A four-level density matrix model is developed to simulate the enhancement and suppression of population and vibrational coherence using such chirped multipulse excitation. The effect of overlap between the excitation and absorption spectra, the degree of chirped excitation and the role of the molecular mode frequency are discussed.

[1] Buckup et al., *JPB* 2008, 41, 074024.

[2] Wand et al., *PCCP* 2010, 12, 2149.

MO 2.3 Mon 12:15 PH/HS1

Photoassociation of hot magnesium atoms by phase-shaped femtosecond pulses — ●WOJCIECH SKOMOROWSKI¹, LIAT LEVIN², LEONID RYBAK², RONNIE KOSLOFF³, CHRISTIANE P. KOCH¹, and ZOHAR AMITAY² — ¹Theoretische Physik, Universität Kassel, Heinrich-Plett-Str. 40, 34132 Kassel, Germany — ²The Shirlee Jacobs Femtosecond Laser Research Laboratory, Schulich Faculty of Chemistry, Technion-Israel Institute of Technology, Haifa 32000, Israel — ³Fritz Haber Research Centre and The Department of Physical Chemistry, Hebrew University, Jerusalem 91904, Israel

One of the long-standing goals in the field of coherent control is the

control of photo-induced bimolecular chemical reactions. Realizing this goal will create a new type of photochemistry with selective control of yields and branching ratios. Shaped laser pulses can act there as special catalysts which drive molecular process to a desired channel. Here we show coherent control of bond making, a milestone on the way to the control of photo-induced chemical reactions. The control is demonstrated in the process of multiphoton photoassociation of hot magnesium atoms by phase-shaped femtosecond laser pulses. We find the yield of observed Mg₂ molecules to be strongly enhanced for positively chirped pulses and suppressed for negatively chirped pulses. Our fully *ab initio* model, combining electronic structure calculations with quantum molecular dynamics, shows that control is achieved by purification via Franck-Condon filtering coupled with chirp-dependent Raman transitions. The presented results prove that coherent control of binary photo-reactions is feasible even under thermal conditions.

MO 2.4 Mon 12:30 PH/HS1

Quantum optimal control of a carbonyl reaction in an explicit solvent cage using tailored laser pulses — ●DANIEL KEEFER, SEBASTIAN THALLMAIR, and REGINA DE VIVIE-RIEDLE — Department Chemie, LMU München

Influencing the outcome of a chemical reaction is an everyday struggle for chemists. A powerful tool to directly interact with a molecular process is to address its quantum nature, which is achieved by using specifically tailored laser pulses. Theoretically, the tailoring is accomplished using optimal control theory (OCT).

Investigating a chemical process which takes place in solution, a proper theoretical treatment becomes more challenging. Electrostatic and dynamic solvent effects influence the quantum dynamical behaviour during the ultrafast reaction. We present a way to account for these effects in OCT optimizations. Therefore, a QD/MD approach combining quantum dynamics (QD) and classical molecular dynamics (MD) is used. The motion of the explicitly included solvent molecules around the reactant is described by MD. Different solvent cage arrangements are extracted from the MD trajectories. These arrangements alter the potential energy surface for the chemical reaction in different ways. The various solvent cage configurations are included in the Hamiltonian to approximate the thermodynamical distribution of the solvent molecules in the solution. Optimizations are conducted to obtain laser pulses for optimal control of an ensemble of solvent arrangements. Significant effects on the shape of the laser pulses controlling the reaction are observed.

MO 2.5 Mon 12:45 PH/HS1

Phase-controlled polarization decay and line-shape modifications in complex systems — ●KRISTINA MEYER, ZUOYE LIU, NIKLAS MÜLLER, and THOMAS PFEIFER — Max-Planck-Institut für Kernphysik, Saupfercheckweg 1, 69117 Heidelberg, Germany

Recently, our group demonstrated the transformation of Fano to Lorentzian line shapes and vice versa in time-resolved absorption experiments in helium. This was realized by inducing phase changes in the singly and doubly excited states by means of laser pulses, enabling the control of the optical dipole response [1]. Now, we show that this mechanism can be generalized to more complex systems in the liquid phase. For this purpose, we performed transient-absorption measurements in the dye molecule IR144 dissolved in methanol. By applying 7-fs short NIR laser pulses significant modifications of the IR144 absorption spectrum could be observed. In order to investigate if the measured line-shape changes could originate from the same Fano-phase formalism as derived for the case of helium, we carried out a numerical simulation. The extremely good qualitative agreement of simulation and experiment proves the universal applicability of the phase-control mechanism to complex systems.

[1] C. Ott et al., *Science* 340, 716 (2013)

MO 3: Femtosecond Spectroscopy 1

Time: Monday 14:30–16:30

Location: PH/HS1

Invited Talk

MO 3.1 Mon 14:30 PH/HS1

Vibrational coherence in excited electronic states studied with multidimensional time-resolved spectroscopy — TIAGO BUCKUP and ●MARCUS MOTZKUS — Physikalisch-Chemisches Institut, Ruprecht-Karls Universität, D-69120 Heidelberg, Germany

Multidimensional femtosecond time-resolved vibrational coherence spectroscopy allows one to studying the evolution of vibrational coherence in electronic excited states. Methods like pump-DFWM and pump-IVS combines an initial ultrashort laser pulse with a nonlinear probing sequence to re-induce vibrational coherence exclusively in the excited states. By carefully exploiting specific electronic resonances, vibrational coherence from 0 cm⁻¹ over 2000 cm⁻¹ can be detected and its evolution can be mapped. This talk focuses on the observation and mapping of high-frequency vibrational coherence for all-trans biological polyenes like lycopene, retinal and retinal Schiff base. We discuss the role of molecular symmetry in the vibrational coherence activity in the S1 electronic state and the interplay of coupling between electronic states and vibrational coherence.

[1] T. Buckup and M. Motzkus, *Annual. Rev. Phys. Chem.* 65 (2014) 39.

MO 3.2 Mon 15:00 PH/HS1

Unraveling photochemical reaction pathways of diphenylcarbene in solvent mixtures — ●JOHANNES KNORR¹, SEBASTIAN SCHOTT², PAOLO COSTA³, WOLFRAM SANDER³, and PATRICK NUERNBERGER¹ — ¹Physikalische Chemie II, Ruhr-Universität Bochum, 44780 Bochum — ²Institut für Physikalische und Theoretische Chemie, Am Hubland, Universität Würzburg, 97074 Würzburg — ³Organische Chemie II, Ruhr-Universität Bochum, 44780 Bochum

The primary reaction pathways of singlet diphenylcarbene (DPC) in the presence of a solvent can be summarized as an interplay of an intersystem crossing to the triplet state (e.g., in neat acetonitrile) and the formation of an ether product (in alcohols) which can either be formed by reaction with an alcohol in a concerted or stepwise manner or via a short-lived cation resulting from an ultrafast intermolecular proton-transfer reaction [1]. Recent studies on DPC embedded in argon matrices at low temperatures revealed dramatic changes in the reactivity when the carbene environment was modified by small amounts of methanol dopant molecules [2]. Connecting these findings with experiments in the liquid phase at room temperature, we employ femtosecond transient-absorption spectroscopy in the visible and ultraviolet regime to unravel the reactivity of DPC in solvent mixtures. Our studies corroborate that the dynamics are far from a linear combination of those observed in neat solvents, with the efficiency of different reaction channels varying significantly in dependence on the solvent mixing ratio.

[1] J. Peon et al., *J. Am. Chem. Soc.* 2002, 124, 6428-6438

[2] P. Costa and W. Sander, *Angew. Chem.* 2014, 53, 5122-5125

MO 3.3 Mon 15:15 PH/HS1

Ultrafast Dynamics of the Low-Temperature Phase of MEH-PPV — ●CRISTINA CONSANI¹, FEDERICO KOCH¹, FABIAN PANZER², THOMAS UNGER², ANNA KÖHLER², and TOBIAS BRIXNER¹ — ¹Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg — ²Lehrstuhl Experimentalphysik II, Universität Bayreuth, Universitätsstraße 30, 95447 Bayreuth

Understanding the effect of structure and aggregation on exciton transport in polymers is relevant for the design of functional artificial systems for applications in organic photovoltaics.

Here we investigate the process of energy transfer in the low-temperature phase of MEH-PPV, a planarized aggregated phase characterized by an increased conjugation length as compared to the coiled room-temperature phase. By combining transient absorption and coherent two-dimensional spectroscopy we identify the characteristic time scales of energy transfer within the aggregate. Additionally, the possibility to retrieve information on the exciton diffusion from the power dependence of the investigated signal will be discussed.

MO 3.4 Mon 15:30 PH/HS1

Photoelectron Circular Dichroism from Multiphoton Ionization with Femtosecond Laser Pulses — CHRISTIAN LUX¹,

●ALEXANDER KASTNER¹, STEFANIE ZÜLLIGHOVEN¹, TOM RING¹, CRISTIAN SARPE¹, ARNE SENFTLEBEN¹, MATTHIAS WOLLENHAUPT², and THOMAS BAUMERT¹ — ¹Universität Kassel, Institut für Physik und CINSaT, D-34132 Kassel, Germany — ²Carl von Ossietzky Universität Oldenburg, Institut für Physik, D-26129 Oldenburg, Germany

The asymmetry of photoelectron angular distributions from randomly oriented enantiomers of chiral molecules in the ionization with circularly polarized light arises in forward/backward direction with respect to the light propagation. This effect was termed Photoelectron Circular Dichroism (PECD) and so far investigated using synchrotron radiation [1]. In our recent publication [2] we demonstrated that PECD is accessible via a Resonance Enhanced Multi-Photon Ionization (REMPI) using femtosecond laser pulses. We observed highly structured asymmetries in the range of $\pm 10\%$. Attributed to the MPI high order odd Legendre polynomials appear in the measured PECD. In this talk we show our recent findings in above-threshold ionization and enantiomeric purity studies on bicyclic Ketones. A first test on molecular modification on Phenylethanol is demonstrated. The strength of PECD can be determined by quantitative measures [3].

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

[2] C. Lux et al., *Angew. Chem. Int. Ed.* 51, 5001-5005 (2012)

[3] C. Lux et al., *ChemPhysChem*, DOI:10.1002/cphc.201402643

MO 3.5 Mon 15:45 PH/HS1

Chiral Distinction via Femtosecond Mass Spectrometry with a Twin Peak Ion Source — CHRISTIAN LUX¹, ●TOM RING¹, STEFANIE ZÜLLIGHOVEN¹, ALEXANDER KASTNER¹, CRISTIAN SARPE¹, ARNE SENFTLEBEN¹, MATTHIAS WOLLENHAUPT², and THOMAS BAUMERT¹ — ¹Universität Kassel, Institut für Physik und CINSaT, D-34132 Kassel — ²Carl von Ossietzky Universität Oldenburg, Institut für Physik, D-26129 Oldenburg

Circular dichroism (CD) in laser mass spectrometry gives access to the distinction of chiral molecules in the gas phase [1,2]. A twin mass peak setup allows circumventing shot-to-shot fluctuations in laser pulse intensity, gas density or ion detection. Two foci with a small spatial displacement result in time-separated mass spectra. A change in helicity from focus to focus implements a self-referencing system. Using nanosecond laser pulses a back reflecting setup [3] provides the desired characteristics. Due to optical dispersion, this does not work with ultra-short laser pulses. Hence, we introduced an in-line setup applicable for femtosecond laser pulses. In this contribution, we show the advantages of the new optical setup and present our first results of mass-selective chiral analysis via time of flight mass spectrometry.

[1] Titze, Zollitsch, Heiz, Boesl: *ChemPhysChem* 2014, 15, 2762-2767

[2] Horsch, Urbasch, Weitzel: *Chirality* 2012, 24, 684-690

[3] Logé, Boesl: *ChemPhysChem* 2011, 12, 1940-1947

MO 3.6 Mon 16:00 PH/HS1

The photoinduced ring closure of an o-acylbenzaldehyde - Intricate kinetics deciphered by femtosecond spectroscopy and quantum chemistry — ●SASCHA FRÖBEL, LAURA BUSCHHAUS, TORBEN VILLNOW, OLIVER WEINGART, and PETER GILCH — Heinrich-Heine-Universität Düsseldorf, Germany

The photoinduced ring closure of o-acylbenzaldehydes has been under investigation for decades. Nevertheless, the course of the reaction is not yet completely understood. This can be attributed to the fact that it contains multiple ultrafast processes, which heretofore could not be resolved.

We combined femtosecond absorption techniques and stimulated Raman spectroscopy (FSRS) with quantum chemical computations to study the photoreaction of o-acetylbenzaldehyde in acetonitrile [1]. It turned out that the photochemistry and -physics of this compound are rather complex, involving at least five kinetic processes within the first two nanoseconds after excitation. By FSRS, one of these processes was identified as an intramolecular hydrogen transfer yielding a ketene intermediate. Afterwards the photoproduct, 3-methylphthalide, is formed via an additional intermediate with a lifetime of more than 100 microseconds.

[1]S. Fröbel et al., *Phys.Chem.Chem.Phys.* 2015, 17, 376-386.

MO 3.7 Mon 16:15 PH/HS1

Ultrafast photophysics of a DNA intercalated psoralen — SASCHA FRÖBEL, ANNA REIFFERS, and PETER GILCH — Heinrich-Heine-Universität Düsseldorf, Germany

After we have studied the formation of photolesions within DNA in the past (see e.g. [1]), we have now extended our studies to photolesions induced by intercalated compounds.

A model system for such compounds are psoralens. Psoralens are heterocyclic natural compounds with various applications in the research lab. Apart from this they are primarily known for their use in the treatment of common skin disorders like psoriasis and vitiligo (PUVA (psoralen + UV-A light) therapy). Their function in PUVA therapy is correlated to their intercalation into DNA. Upon photo ex-

citation, intercalated psoralens form [2+2] cycloadducts with thymines and thus damage the host cells. However, the ultrafast photochemical and -physical processes after excitation are still fully unknown.

We have studied the interactions of an intercalated psoralen (4'-aminomethyl-4,5',8-trimethylpsoralen, AMT) with DNA by means of femtosecond transient absorption for the first time. In DNA the fluorescence lifetime is reduced to 4 ps as compared to 1.4 ns for free AMT. This prohibits the population of triplet states. Instead, an unanticipated intermediate with a lifetime of 30 ps is formed, which is assigned to an electron transfer product. Hereby, the DNA acts as an electron donor.

[1]W.J. Schreier et al., Science 2007, 315, 625./G. Ryseck et al., Chem.Phys.Chem. 2011, 12, 1880.

MO 4: Cold Molecules 1

Time: Monday 14:30–16:30

Location: PH/SR106

MO 4.1 Mon 14:30 PH/SR106

Trapping of polar molecules in a segmented electrostatic quadrupole guide — THOMAS GANTNER, JANNIK LUHN, XING WU, SOTIR CHERVENKOV, MARTIN ZEPPENFELD, and GERHARD REMPE — Max-Planck-Institut für Quantenoptik, 85748 Garching, Germany

We present a simple and robust method for trapping of neutral polar polyatomic molecules in an electrostatic quadrupole guide. A beam of polar molecules from a liquid-nitrogen-cooled nozzle is injected into an electrostatic quadrupole guide [1] consisting of four consecutive segments. One of those segments is used as a trap and thus intrinsically provides a two-dimensional transverse confinement for the molecules. To capture the molecules in the third dimension, along the guide, the segments before and after the trap are switched in a way to provide electrostatic potential barriers in the longitudinal direction. Thereby, we have achieved trapping of CH₃F molecules with a trap lifetime of about 170 ms. By implementing a more advanced guide switching scheme, we expect to boost the absolute number of trapped molecules as well as the trapping lifetime. As electrostatic guiding is well-established for various polar polyatomic molecules [2], the trap-in-guide technique is easily applicable to other species, providing a means to study electrically guided molecules, e.g., probing them spectroscopically.

References

- [1]S.A. Rangwala et al., Phys. Rev. A 67, 043406 (2003)
- [2]C. Sommer et al., Phys. Rev. A 82, 013410 (2010)

MO 4.2 Mon 14:45 PH/SR106

Internal state thermometry of buffer-gas cooled and electrically guided polar molecules — XING WU, THOMAS GANTNER, SOTIR CHERVENKOV, MARTIN ZEPPENFELD, and GERHARD REMPE — Max-Planck-Institut für Quantenoptik, Hans-Kopfermann-Str. 1, D-85748 Garching, Germany

We present a general technique for detecting the internal states of polyatomic molecules after cryogenic buffer-gas cooling [1] and electrostatic guiding [2]. Bright beams of polar molecules produced by a cryogenic buffer-gas cell are extracted by electric quadrupole guiding, and delivered to a region of homogeneous offset electric field, where different Stark sub-levels are split. Applying an RF field resonant with a particular splitting drives $\Delta M = \pm 1$ transitions for the selected rotational state. Only molecules remaining in low-field-seeking states are further guided to a quadrupole mass spectrometer for detection. The population in each rotational state can be derived from this depletion signal. After taking into account the velocity distribution in the guide and the Stark shift of each state, internal temperatures can be assigned to the guided molecular beams. This method is extremely simple to implement and compatible with the existing electric guiding technique. Application to a variety of molecular species as well as for a range of parameters for the buffer-gas source is shown.

- [1] L.D. van Buuren et al., Phys. Rev. Lett. **102**, 033001 (2009)
- [2] S.A. Rangwala et al., Phys. Rev. A **67**, 043406 (2003)

MO 4.3 Mon 15:00 PH/SR106

IR and UV-NIR absorption spectroscopy of matrix isolated C₇₀^{+/-}: theory breaks down. — DMITRY STRELNIKOV, BASTIAN KERN, ARTUR BÖTTCHER, PATRICK WEIS, and MANFRED M. KAPPES — Institute of physical chemistry II, KIT, Fritz-Haber-Weg 2, Karl-

sruhe, Germany

Fullerene C₇₀ ions have recently become of interest to the astronomy community and are also relevant in the field of organic photovoltaics. C₇₀⁺ ions were mass-selectively deposited into a neon matrix at 5 K. Like in the case of C₆₀⁺ deposition [1], soft landing into neon is associated with some charge exchange processes such that C₇₀⁺ as well as resulting C₇₀ and C₇₀⁻ can be probed simultaneously. In contrast to a very good coincidence of the experimental and DFT-calculated IR spectra of C₆₀^{+2+/-} [1, 2], DFT predictions for C₇₀^{+/-} IR absorptions strongly deviate from our measurements. A possible explanation for this could be low lying electronically excited states of C₇₀^{+/-} in the vicinity of vibrational energy levels. The corresponding non-Born-Oppenheimer case is likely of significant interest to theory.

References:

1. B. Kern, D. Strelnikov, P. Weis, A. Böttcher, M. M. Kappes. J. Phys. Chem. A 2013, 117, 8251–8255.
2. B. Kern, D. Strelnikov, P. Weis, A. Böttcher, M. M. Kappes. J. Phys. Chem. Lett. 2014, 5, 457–460.

MO 4.4 Mon 15:15 PH/SR106

Rotational state-changing cold collisions of hydroxyl ions with helium — DANIEL HAUSER, SEUNGHYUN LEE, FABIO CARELLI, STEFFEN SPIELER, OLGA LAKHMANSKAYA, ERIC ENDRES, SUNIL KUMAR, FRANCO GIANTURCO, and ROLAND WESTER — Institute for Ion Physics and Applied Physics, University of Innsbruck, 6020 Innsbruck, Austria

Sympathetic collisions with cold atoms and atomic ions are widely used to prepare translationally cold molecules and molecular ions. Inelastic collisions with neutral atoms have proven to be a general approach to cool internal degrees of freedom [1,2]. Here we present a new scheme to measure the absolute quantum scattering rate coefficients for the rotationally inelastic collision of hydroxyl anions and their deuterium-containing counterparts upon interaction with helium in a multipole radio-frequency ion trap. The measured rates and the ab initio quantum scattering calculations agree very well with each other. With the methods developed, improved quantum state-preparation of molecular ions for precision spectroscopy or quantum information research is achieved.

- [1] R. Otto, A. von Zastrow, T. Best and R. Wester, 2013 *Physical Chemistry Chemical Physics* **15** 612-618 (2013)
- [2] A. K. Hansen, O. O. Versolato, L. Klosowski, S. B. Kristensen, A. Gingell, M. Schwarz, A. Windberger, J. Ullrich, J. R. C. Lopez-Urrutia, M. Drewsen, *Nature* **508**, 76-79 (2014).

MO 4.5 Mon 15:30 PH/SR106

The Characterization of Complex Carbohydrates in Liquid Helium Nanodroplets using IR Spectroscopy — CHRISTIANE STACHL¹, JOHANNA HOFMANN¹, HEUNG SIK HAHM², PETER SEEBERGER², KEVIN PAGEL¹, and GERT VON HELDEN¹ — ¹Fritz-Haber-Institut der MPG, Berlin, Germany — ²Max-Planck-Institut für Kolloid- und Grenzflächenforschung, Potsdam, Germany

Complex carbohydrates are typically characterized using mass spectrometry (MS)-based techniques. However, because the atomic composition of entire classes of monosaccharide building blocks is identical,

it has proven difficult to differentiate the molecular structure of these biomolecules based on MS data alone. To overcome this fundamental problem, ion mobility-MS has been used to separate carbohydrates of identical mass but different structure according to their collision cross sections [1]. Conversely, it also is possible to use gas-phase infrared spectroscopy to gain additional information regarding the structure of complex carbohydrates. Ideal matrices in which to do this are liquid helium doplets, which are isothermal at 0.37 K, interact only weakly with an embedded molecule, and are transparent over a wide spectral range [2]. Here, we present the cold-ion IR spectroscopy of complex carbohydrates doped in liquid helium droplets using the Fritz-Haber-Institut free electron laser. We show that a nano-cryostat environment is an idyllic method to better resolve differences in the conformations of complex carbohydrates. [1] Pagel, K., Harvey, D. J., *Anal. Chem.*, 2013, 85, 5138. [2] Toennies, J. P., Vilesov, A. F., *Angew. Chem. Int. Ed.*, 2004, 43, 2622.

MO 4.6 Mon 15:45 PH/SR106

The cross-over from free to hindered rotation in liquid helium — LUIS G. MENDOZA LUNA¹, NAGHAM SHILTAG¹, MARK J. WATKINS¹, ●KLAUS VON HAEFTEN¹, NELLY BONIFACI², and FREDERIC AITKEN² — ¹Department of Physics and Astronomy, University of Leicester, Leicester, LE1 7RH, UK — ²G2ELab-CNRS Equipe MDE 25 Av. des Martyrs BP 166, 38042 Grenoble Cedex 9 France

The observation of free rotation of single molecules in superfluid helium droplets 20 years ago has caused considerable interest. To better understand free rotation in quantum fluids we have investigated the rotational motion of single molecules in bulk liquid helium as a function of hydrostatic pressure and temperature using fluorescence spectroscopy in the visible region. A corona discharge was employed to generate electronic excitations in liquid helium. He₂^{*} excimers formed and decayed via cascade-radiative transitions to the ground state. During their short life the excimers do not aggregate, hence, molecular interactions in bulk liquid helium can be conveniently probed. At low hydrostatic pressures well-resolved rotational lines, indicating free rotation of He₂^{*} within liquid helium, are observed. When the hydrostatic pressure is increased the rotational lines broaden until they disappear around 6 bar. The line width depends distinctly on pressure and rotational excitation and is attributed to the reduced space available to the molecule to perform rotational motion. Our results are contrasted with the findings of molecular infrared spectroscopy in helium droplets. The microscopic origin of free molecular rotation in liquid helium is discussed.

MO 4.7 Mon 16:00 PH/SR106

Traveling-wave deceleration of SrF molecules — ●SREEKANTH MATHAVAN, JOOST VAN DEN BERG, CORINE MEINEMA, ARTEM ZAPARA, KLAUS JUNGMANN, RONNIE HOEKSTRA, and STEVEN HOEKSTRA — University of Groningen, The Netherlands

We work on the development of methods to cool and trap selected diatomic molecules suited for precision measurements, exploiting the long coherence time offered by cold, trapped molecules.

Traditional stark decelerators are inefficient for the deceleration of heavy diatomics such as SrF, due to instabilities. We have built a traveling-wave decelerator in our lab for the deceleration of heavy diatomics, which is inherently stable. We are improving the molecular source in order to achieve optimal rotational cooling and molecular density. Following the deceleration, we will laser cool the molecules to prepare them for a parity violation measurement.

We present the status of the experiment and present the first results on the deceleration of SrF molecules in a traveling-wave decelerator

MO 4.8 Mon 16:15 PH/SR106

Superradiance of Organic Molecules Attached to the Surface of Solid Neon Cluster — ●SHARAREH IZADNIA, MARKUS MÜLLER, AARON LAForge, and FRANK STIENKEMEIER — Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str.3, 79104 Freiburg

Superradiance [1] is a collective effect where all excited states simultaneously emit radiation. This can lead to a reduced effective lifetime and an enhancement in the radiative intensity, which has been observed almost universally in weakly interacting systems such as hot dense gases [2] and films [3] and Bose-Einstein-Condensates [4]. Recently, we observed a new superradiative system where large immobile chromophores (e.g. tetracene, pentacene, PTCDA) attached to the surface of neon clusters exhibit the characteristic lifetime shortening of superradiance.

In this talk, we will present absorption spectra, emission spectra, and fluorescence lifetime measurements which indicate the first observation of superradiance in such a system.

[1] R. H. Dicke, *Phys. Rev.* 93, 99 (1954).

[2] N. Skribanowitz, I. P. Herman, J. Macgilli, and M. S. Feld, *Phys. Rev. Lett.* 30, 309 (1973).

[3] M. Müller, A. Paulheim, A. Eisfeld, and M. Sokolowski, *J. Chem. Phys.* 139, 044302 (2013).

[4] D. Schneble, Y. Torii, M. Boyd, E. W. Streed, D. E. Pritchard, and W. Ketterle, *Science* 300, 475 (2003).

MO 5: Posters 1: Novelties in Molecular Physics

Time: Monday 17:00–19:00

Location: C/Foyer

MO 5.1 Mon 17:00 C/Foyer

Hartree-Fock calculation of the differential photoionization cross sections of small Li clusters — ●SERGEY A GALITSKIY¹, ANTON N ARTEMYEV¹, KARI JÄNKÄLÄ², BORIS M LAGUTIN³, and PHILIPP V DEMEKHIN¹ — ¹Institut für Physik, Universität Kassel, Heinrich-Platt-Str. 40, 34132 Kassel, Germany — ²Department of Physics, University of Oulu, P.O. BOX 3000, 90014 Oulu, Finland — ³Research Institute of Physics, Southern Federal University, Stachki av. 194, 344090 Rostov-on-Don, Russia

Cross sections and angular distribution parameters for the single-photon ionization of all electron orbitals of Li_{2–8} are systematically computed in a broad interval of the photoelectron kinetic energies for the energetically most stable geometry of each cluster. Calculations of the partial photoelectron continuum waves in clusters are carried out by the Single Center method within the Hartree-Fock approximation. We study photoionization cross sections per one electron and analyze in some detail general trends in the photoionization of inner and outer shells with respect to the size and geometry of a cluster. The present differential cross sections computed for Li₂ are in a good agreement with the available theoretical data, whereas those computed for Li_{3–8} clusters can be considered as theoretical predictions.

MO 5.2 Mon 17:00 C/Foyer

Optical spectroscopy and structures of photo dissociated doped silicon clusters — ●BERTRAM K.A. JAEGER, JANINA LEBENDIG, NGUYEN X. TRUONG, ANDRE FIELICKE, and OTTO DOPFER — IOAP, TU Berlin, Germany

Doped Si clusters with their great variety in physical and chemical properties are promising candidates for optoelectronics, sensors or medicine. We study the photodissociation of C, N and O doped Si clusters and compare the spectra with quantum chemical calculations. A laser vaporization source produces ionic clusters, which are then irradiated with a tunable visible laser in the range from 410 to 580 nm. Photo-induced dissociation of the cluster changes the mass spectrum, which is recorded by a reflectron time-of-flight mass spectrometer. Calculated absorption spectra are compared to experimental data to access geometric or electronic parameters. With the help of genetic and basin-hopping algorithms the most stable and low-energy isomers are identified. Results are to be verified by existing studies of IR-UV two color ionization of neutral and doped Si clusters [1]. The basic principle of the experimental setup is shown with pristine and Ar-tagged Au₄₊ clusters. [1] N.X. Truong et al., *Phys. Chem. Chem. Phys.*, 2014, 16, 40, 22364-22372

MO 5.3 Mon 17:00 C/Foyer

A molecular movie of Interatomic Coulombic Decay in NeKr — ●FLORIAN TRINTER¹, TSVETA MITEVA², MIRIAM WELLER¹, SEBASTIAN ALBRECHT¹, ALEXANDER HARTUNG¹, MARTIN RICHTER¹, JOSHUA WILLIAMS¹, AVERELL GATTON³, BISHWANATH GAIRE³, THORSTEN WEBER³, JAMES SARTOR⁴, ALLEN LANDERS⁴, BEN BERRY⁵, VASIL STUMPF², KIRILL GOKHBERG², TILL JAHNKE¹, and REINHARD DÖRNER¹ — ¹Institut für Kernphysik, Goethe-Universität, 60438 Frankfurt am Main, Germany — ²Theoretische Chemie, Physikalisch-Chemisches Institut, Universität Heidelberg, 69120 Hei-

delberg, Germany — ³Lawrence Berkeley National Laboratory, Chemical Sciences Division, Berkeley, California 94720, USA — ⁴Department of Physics, Auburn University, Auburn, Alabama 36849, USA — ⁵J. R. Macdonald Laboratory, Department of Physics, Kansas State University, Manhattan, Kansas 66506, USA

During the last 15 years a novel decay mechanism of excited atoms has been discovered and investigated. This so called "Interatomic Coulombic Decay" (ICD) involves the chemical environment of the electronically excited atom or molecule: the excitation energy is transferred to a neighbor of the initially excited particle usually ionizing that neighbor. It turned out that ICD is a very common decay route in nature as it occurs across van der Waals and hydrogen bonds. The time evolution of ICD is predicted to be highly complex, as its efficiency strongly depends on the distance of the atoms involved and this distance typically changes during the decay. Here we present a direct measurement of the temporal evolution of ICD using a novel experimental approach.

MO 5.4 Mon 17:00 C/Foyer

Enantiomeric excess determination of Chiral Molecules from Multiphoton Ionization with Femtosecond Laser Pulses — CHRISTIAN LUX, •STEFANIE ZÜLLIGHOVEN, ALEXANDER KASTNER, TOM RING, CHRISTIAN SARPE, ARNE SENFTLEBEN, and THOMAS BAUMERT — University of Kassel, Institute of Physics and CINSaT, D-34132 Kassel, Germany

Photoelectron Circular Dichroism (PECD) shows asymmetries in the electron emission from chiral enantiomers relative to the light propagation direction and was so far investigated using synchrotron radiation [1]. The magnitude of PECD is several orders larger than typically chiroptical asymmetries. We have demonstrated that PECD on randomly oriented chiral enantiomers is accessible via a 2+1 REMPI (Resonance Enhanced Multi-Photon Ionization) using femtosecond laser pulses. We detected highly structured asymmetries in the $\pm 10\%$ regime [2]. In this contribution we present our recent findings on the bicyclic Ketones Camphor, Norcamphor and Fenchone [3]. From the results on variation of the laser intensity, we conclude an underlying dissociative ionization. A quantification of different enantiomeric mixtures reveals the sensitivity of the PECD to the enantiomeric excess. The enantiomeric excess in mixtures of R- and S-Fenchone can be distinguished in the 1% regime.

[1] I. Powis *Adv. Chem. Phys.* 138, 267-329 (2008)

[2] C. Lux et al., *Angew. Chem. Int. Ed.* 51, 5001-5005 (2012)

[3] C. Lux et al., *ChemPhysChem*, DOI: 10.1002/cphc.201402643 (2015)

MO 5.5 Mon 17:00 C/Foyer

Extended quantum jump description of vibronic two-dimensional spectroscopy — •JULIAN ALBERT, MARTIN KESS, MIRJAM FALGE, JOHANNES G. WEHNER, and VOLKER ENGEL — Institut für Physikalische und Theoretische Chemie, Emil-Fischer-Str. 42, Universität Würzburg, 97074 Würzburg, Germany

We calculated two-dimensional vibronic spectra for model systems involving two electronic molecular states. The coupling to a bath is simulated using a quantum-jump approach. For the latter, we use a method introduced by Makarov and Metiu [1] which includes an explicit treatment of dephasing. In this way it is possible to characterize the influence of dissipation and dephasing on the 2D-spectra.

[1] D. E. Makarov and H. Metiu, *J. Chem. Phys.* 111, 10126 (1999).

MO 5.6 Mon 17:00 C/Foyer

Acceleration of Singlet Fission in an Aza-Derivative of TIPS-Pentacene — •JULIA HERZ¹, FABIAN PAULUS², JENS ENGELHART², TIAGO BUCKUP¹, UWE BUNZ², and MARCUS MOTZKUS¹ — ¹Physikalisch-Chemisches Institut — ²Organisch-Chemisches Institut, Ruprecht-Karls-Universität, D-69120 Heidelberg, Germany

Singlet fission plays a prominent role in raising the quantum efficiency of organic solar cells. In this overall spin-conserved process two molecules in the triplet state T1 are formed by investing just one photon. Pentacene is known to undergo singlet fission and is an attractive starting compound to develop new chromophores with promising photo-physico-chemical qualities. By means of ultrafast transient absorption measurements with high time resolution, we provide a detailed picture of the excited state dynamics of TIPS-pentacene [1], an important, soluble derivative of pentacene. A kinetic model was derived by carrying out a global target analysis. Furthermore, we found that a carbon to nitrogen substitution has a high impact on the triplet formation and leads to faster initial dynamics. The chemical modification

can accelerate singlet fission in the aza-derivative by almost a factor of two. A faster relaxation from the singlet to triplet manifold implies a higher efficiency, because other relaxation channels are avoided. A stronger triplet signal in the near infrared spectral region relative to that in the visible indicates a higher quantum yield when compared to TIPS-pentacene, making the more air-stable aza-derivatives promising for organic electronics applications. [1] Herz et al, *JPC Let.* 5 (2014) 2425.

MO 5.7 Mon 17:00 C/Foyer

Optimization of the measurement method of fs pump-probe experiment by compressed sensing — •DANIEL UHL, LUKAS BRUDER, MARCEL BINZ, MARCEL MUDRICH, AARON LAForge, DAVID GROSS, and FRANK STIENKEMEIER — Physikalisches Institut, Universität Freiburg, Germany

Deducing the spectrum of a fs spectroscopy experiment generally requires sampling the signal in the time domain at a rate that suffices the Shannon-Nyquist-Theorem. This boundary condition can result in very long acquisition times especially in multi-dimensional spectroscopy setups where even more data points are required. Compressed sensing reconstructs a signal by exploiting the sparsity of the signal in the frequency domain and allows for sampling far below the Shannon-Nyquist-Theorem in the time domain, while yielding the same information content. In view of combining this method with 2D spectroscopy we are investigating at first its applicability to fs pump-probe spectroscopy. We have investigated quantum beat spectra of atomic vapors and a simple diatomic molecule by analyzing simulated as well as experimental data with this method.

MO 5.8 Mon 17:00 C/Foyer

Realization of Ultrafast Logic Gate for Reversible Computation by Nonlinear Optical Techniques — •MEHDI MOHAMMAD KAZEMI, ALIREZA MAZEHERI TEHRANI, TAHIR ZEB KHAN, and ARNULF MATERNY — Jacobs University, Campus Ring 1, 28759 Bremen, Germany

A Toffoli gate (CCNOT gate) is a universal reversible logic gate, from which all other reversible gates can be constructed. It has a three-bit input and output. The goal of our work was to realize a Toffoli gate where all inputs and outputs are realized optically, which allows for ultrafast switching processes. We demonstrate experimentally that a Toffoli logic gate can be based on nonlinear multi-wave interactions of light with matter. Using femtosecond laser pulses, the all-optical Toffoli gate is making use of the coherence of the optical signal produced via the nonlinear optical process. Sum frequency (SF) and second harmonic (SH) generations are combined in such a way so as to yield the complete truth table of the universal reversible logic gate.

MO 5.9 Mon 17:00 C/Foyer

Time-dependent photoelectron spectroscopy of all-trans retinal in liquid micro-jet — •IASON KATECHIS¹, KATHRIN AZIZ-LANGE^{1,2}, MARTIN ECKSTEIN¹, JOHAN HUMMERT¹, FRANZISKA BUCHNER¹, ANDREA LÜBCKE¹, and OLEG KORNILOV¹ — ¹Max Born Institute Berlin, Germany — ²present address: Helmholtz Zentrum Berlin, Germany

The isomerization of all-trans-retinal, the primary step in vision, has been studied in great detail. Nevertheless the ordering of its excited states, their lifetimes and how these are affected by different solvent environments remain unclear. Time-resolved femtosecond spectroscopy promises to shed light on these questions, however several studies performed so far report contradictory results on the lifetimes observed in experiments and this leads to an ambiguity in the choice of a photo-physical model.

In our study we employ time-resolved photoelectron spectroscopy of retinal in a liquid micro-jet for different solvents. We observe that it is important to investigate different data analysis strategies since they can lead to contradicting results. We hence compare methods including global fitting and singular value decomposition (SVD) along with more flexible photophysical models than those assumed so far in order to get deeper insight into the underlying mechanisms.

MO 5.10 Mon 17:00 C/Foyer

Coherent and incoherent contributions to the carrier-envelope phase control of wave packet localization in quantum double wells — •KILIAN HADER — Institut für Physikalische und Theoretische Chemie, Emil-Fischer-Str. 42, Universität Würzburg, 97074 Würzburg, Germany

We study laser excitation processes in a double well potential. The possibility to influence localization via the carrier-envelope phase (CEP) of a laser pulse is investigated for various situations which differ in the nature of the initial state prior to the laser interactions. In more detail, the CEP-dependence of asymmetries in the case where initially the system is described by localized wave packets, eigenstates or incoherent mixtures are calculated and interpreted within time-dependent perturbation theory. It is investigated which contributions to the asymmetry exist and how they can be modified to reveal a more or less pronounced CEP-effect.

[1] K. Hader, V. Engel, J. Chem. Phys. 140, 184316 (2014)

MO 5.11 Mon 17:00 C/Foyer

Dissociative electron attachment in biologically relevant molecules — ●MARVIN WEYLAND^{1,2}, ALEXANDER DORN², HANS RABUS¹, XUEGUANG REN^{1,2}, THOMAS PFLÜGER^{1,2}, and WOON YONG BAEK¹ — ¹Physikalisch-Technische Bundesanstalt, Braunschweig, Germany — ²Max-Planck-Institute for Nuclear Physics, Heidelberg, Germany

Dissociative electron attachment (DEA) is presumed to be a large contributor to radiation damage in biological tissue and, therefore, has gained increased attention during the last decade. We set up a COLTRIMS-type instrument, adapted for negative ion detection to measure emission angles and energies of anions created in DEA-processes. Using a photoemission electron source we reach an impact energy resolution of 200 meV at about 1 μ A peak current, thereby improving energy resolution compared to previous setups. First experiments have been performed with ammonia, investigating DEA in the monomer and small clusters. Advancing towards biologically relevant molecules we investigated furan. This liquid target is introduced using a seeded supersonic gas jet. We studied several fragmentation products at the DEA resonance around 6 eV electron impact energy, which should allow a more detailed understanding of the attachment process.

MO 5.12 Mon 17:00 C/Foyer

Dipole-driven dynamics for near threshold electron/positron interactions with DNA/RNA bases — ●FABIO CARELLI¹, JAN FRANZ², and FRANCO A. GIANTURCO^{1,3} — ¹Institute for Ion Physics and Applied Physics, Innsbruck University, 6020 Innsbruck, Austria — ²Department of Atomic, Molecular and Optical Physics, University of Technology, 80-233 Gdansk, Poland — ³Scuola Normale Superiore, 56125 Pisa, Italy

It is well known that when an external ionizing radiation interacts with living organisms, one of the mechanisms responsible for genetic damage involves metastable attachment of secondary low-energy electrons to DNA/RNA bases, while the interactions of low-energy positrons in molecular biological gases or in condensed media has found a widespread range of applications (for example the role of positronium formation/annihilation probabilities in different environments).

For all the above processes, the knowledge of the paths by which the impinging lepton attaches biomolecules is crucial.

We know that for gas-phase rotating polar molecules with supercritical dipoles a finite number of Rydberg-like states involving e^- exists (and for e^+ could exist, being mainly differentiated by the spatial orientation).

The interaction dynamics of DNA/RNA bases (all having large permanent dipoles) with near-threshold collisions involving e^-/e^+ shall be presented and discussed: the aim is suggesting a new formation/stabilization mechanism for charged biomolecules occurring through a more 'gentle' energy release path.

MO 5.13 Mon 17:00 C/Foyer

Cryo spectroscopy of size selected cobalt clusters — ●SEBASTIAN DILLINGER, JENNIFER MOHRBACH, MAXIMILIAN GAFFGA, JOACHIM HEWER, and GERON NIEDNER-SCHATTEBURG — Fachbereich Chemie and Forschungszentrum OPTIMAS, Technische Universität Kaiserslautern, 67663 Kaiserslautern, Germany

We have performed Infrared (Multiple) Photon Dissociation (IR(M)PD) spectroscopy of adsorbed nitrogen on size selected cobalt cluster cations (Co_n^+ , $n = 8 - 17$) at well-defined cryo temperatures. Our setup combines a hexapole ion trap for kinetic studies with a FT-ICR cell for IR(M)PD studies and mass analysis. Both ion traps are cryogenically cooled to temperatures below 30 K. The cold IR(M)PD spectra of the $[\text{Co}_n(\text{N}_2)_1]^+$ clusters reveal well resolved bands. All complexes show single or multiple IR active bands within the range of 2180 to 2290 cm^{-1} (2110 - 2350 cm^{-1} probed). These bands are sig-

nificantly red shifted with respect to the IR inactive stretching mode of free N_2 (at 2359 cm^{-1}). Preliminary ab initio DFT calculations augment the current experiments, failing to provide unambiguous structural conclusions as of now.

MO 5.14 Mon 17:00 C/Foyer

Theoretical description of ultra-long-range Rydberg molecules — ●CHRISTIAN FEY¹, MARKUS KURZ¹, and PETER SCHMELCHER^{1,2} — ¹Zentrum für optische Quantentechnologien, Universität Hamburg — ²Hamburg Centre for Ultrafast Imaging, Universität Hamburg

Ultra-long-range Rydberg molecules are "giant molecules" that consist of a Rydberg atom whose valence electron bounds one or even more ground state atoms by partial wave scattering at equilibrium distances of several 1000 Å. They differ from usual molecules not only by their exotic physical properties (e.g dipole moments $\sim 10^3$ Debye) but also by their theoretical description. Here we review and link the different theoretical methods which are currently employed in the literature to determine the molecular Born-Oppenheimer potential curves. These methods rely either on zero-range Fermi-like pseudopotentials (e.g. bare or regularized delta potentials) or on the use of the Coulomb Green's function inside quantum defect theory.

MO 5.15 Mon 17:00 C/Foyer

Motion manipulation of 4-aminobenzonitrile with microwave fields — ●JACK GRANEEK, SIMON MERZ, THOMAS BETZ, and MELANIE SCHNELL — Max-Planck-Institut für Struktur und Dynamik der Materie at the Center for Free-Electron Laser Science, 22761 Hamburg, Germany

To manipulate the motion of large and complex molecules, or molecules in their ground state it is necessary to employ methods that are compatible with high-field-seeking states. High-field-seeking states are attracted to field maxima, which cannot be realized in free space with static fields. Therefore, motion manipulation of such states requires the use of time-dependent fields. A previous experiment using microwave fields within a resonator achieved an additional deceleration of a pre-decelerated packet of ammonia molecules [1]. Here, we employ a modified experimental setup for the manipulation of a molecular beam of 4-aminobenzonitrile (ABN), a larger and heavier (118 g/mol) molecule, directly from a supersonic expansion. ABN displays a large dipole moment. It is an asymmetric top so also has a more complex rotational structure. In order to predict the AC Stark shift of the ABN rotational levels within our microwave resonator we have developed a numeric simulation. From this we can determine which rotational states are more accessible for focusing with a microwave lens. Here, we will present the results of calculations carried out as well as details on the new experimental set up.

[1] S. Merz, C. Brieger, N. Vanhaecke, G. Meijer, and M. Schnell, Mol. Phys. 111, 1855-1864 (2013).

MO 5.16 Mon 17:00 C/Foyer

Evidence for long-lived collision complexes in scattering of ultracold ground-state molecules — ●KATHARINA LAUBER, EMIL KIRILOV, MANFRED MARK, FLORIAN MEINERT, and HANNS-CHRISTOPH NÄGERL — Institut für Experimentalphysik, Universität Innsbruck, 6020 Innsbruck, Österreich

Ultracold molecules trapped in optical lattice potentials at high densities and prepared in their lowest internal quantum state are an ideal starting point for fundamental studies in physics and chemistry, ranging from novel quantum gas experiments and cold controlled chemistry to quantum simulation. We create ultracold and dense samples of Cs dimer molecules in their rovibrational ground state in an optical lattice with near unity occupation probability at the individual lattice sites. The preparation involves the formation of a Cs Bose-Einstein condensate, the transition to a Mott-insulating state, the formation of Feshbach molecules, and coherent 4-photon ground-state transfer. Lowering the lattice potential along one or two directions allows us to probe the molecules' collisional properties in one- and two-dimensional geometry, respectively. Atoms can also be used as scattering partners. In all cases under investigation we observe rather rapid loss of molecules, in particular when the molecules are in their absolute hyperfine ground state. We attribute such loss to the formation of elastically bound long-lived collision complexes, i.e. the formation of atom-dimer or dimer-dimer two-body complexes, which then undergo a secondary collision with another atom or molecule. We model our data to derive rate coefficients and lifetimes and compare the results to recent predictions.

MO 5.17 Mon 17:00 C/Foyer

A High Resolution Microwave Spectrometer to Study Large Chiral Molecules — ●CHRIS MEDCRAFT^{1,2}, ROBERT WOLF³, and MELANIE SCHNELL^{1,2} — ¹Max-Planck-Institut für Struktur und Dynamik der Materie, Hamburg, Germany — ²Center for Free-Electron Laser Science, Hamburg, Germany — ³Universität Regensburg, Institut für Anorganische Chemie, Regensburg, Germany

A high-resolution, cavity-based Fourier-transform microwave spectrometer is being commissioned in Hamburg. The spectrometer is based around the COBRA design (Coaxially Oriented Beam-Resonator Arrangement^[1]). The higher resolution (ca. 3 kHz) and larger spectral range (6-40 GHz) of this instrument will complement our broadband chirped-pulse FTMW spectrometer^[2] (2-8.5 GHz), allowing for investigations of nuclear quadrupole hyperfine structure and internal rotation. When combined with a source of cold, slow molecules,^[3] transit-time and Doppler broadening is reduced and the enhanced resolution may be able to discriminate the parity violating effects in large chiral molecules such as CpRe(NO)(CO)I (Cp=cyclopentadienyl). The rotational spectrum of the related molecule CpRe(CH₃)(CO)(NO) has been measured using the chirped-pulse FTMW spectrometer showing that the analysis of such large and complicated molecules is feasible.^[4]

^[1]Grabow, Rev. Sci. Instrum., 67, 4072 (1996)

^[2]Schmitz, Shubert, Betz, Schnell, J. Mol. Spec 280 (2012) 77

^[3]Merz, Vanhaecke, Jäger, Schnell, Meijer, Phys. Rev. A 85, (2012) 063411

^[4]Medcraft, Wolf, Schnell Angew. Chem. Int. Ed. 53 (2014) 11656

MO 5.18 Mon 17:00 C/Foyer

Infrared Spectroscopy of Helium Solvated π -conjugated Organic Radicals — ●DANIEL LEICHT, DANIEL HABIG, MATIN KAUFMANN, GERHARD SCHWAAB, and MARTINA HAVENITH — Physikalische Chemie II, Ruhr-Universität Bochum

Helium nanodroplet infrared spectroscopy is a well established experimental technique to study weakly bound complexes as well as reactive species. [1] Superfluid helium hardly interacts with the embedded species, which leads to only small matrix-induced shifts. Recently, different reactive molecules (e.g. organic radicals) have been studied using helium nanodroplet spectroscopy. [2,3] In this work we present some of our latest results regarding π -conjugated radicals. Examples are allyl, benzyl and cyclopentadienyl radicals that are important intermediates in many reactions in e.g. combustion, explosives and in tropospheric chemistry. Apart from studying the bare radical also aggregates with other molecules (e.g. allyl radical + HCl) and reactions at cold temperatures (e.g. allyl radical + NO [2]) can be investigated using our technique.

[1] M. Choi, G. Douberly, T. Falconer, W. Lewis, C. Lindsay, J. Merritt, P. Stiles and R. Miller, International Reviews in Physical Chemistry, 2006, 25, 15-75

[2] D. Habig, D. Leicht, M. Kaufmann, G. Schwaab, M. Havenith, The Journal of Chemical Physics, 141, 044312 (2014)

[3] Jochen Küpper, Jeremy M. Merritt, International Reviews in Physical Chemistry, 26, Iss. 2, 2007

MO 5.19 Mon 17:00 C/Foyer

Precise FTIR Study of Ethylene and Its Isotopomers — OLEG N. ULENIKOV¹, OLGA V. GROMOVA¹, ELENA S. BEKHTEREVA¹, KARL-HEINZ GERICKE², CHRISTOF MAUL², and ●SIGURD BAUERECHEK² — ¹Department of General Physics, Tomsk Polytechnic University, Russia — ²Institut für Physikalische und Theoretische Chemie, TU Braunschweig, Germany

Ethylene is one of the most relevant substances in the study of numerous both pure scientific and applied problems of physics, chemistry, and astrophysics. Ethylene plays an important role in structural chemistry. In particular, its C=C bond length has been chosen as a standard in the discussion of molecular structure. The present work is part of a systematic analysis of the spectra of ethylene and its isotopomers. We report recent results of high resolution studies of the 12C₂H₄, 13C₂H₄, 12C₂H₃D, 12C₂H₂D₂-trans, 12C₂H₂D₂-cis, and 12C₂H₂D₂-as ethylene isotopic species. Precise infrared spectra were measured with a FTIR spectrometer Bruker 120HR at different temperatures, pressures and path lengths. Spectra have been recorded in the region of the 1200-6000 cm⁻¹. Transitions in all the recorded spectra have been assigned and further analysis was made in the frame of the model which takes into account numerous resonance interactions in the sets of bands located in the corresponding spectral regions. The obtained sets of spectroscopic parameters allow to use the obtained information both for a

further precise analysis of the line strengths and shape of spectral lines of ethylene and its isotopomers, and also for a correct determination of the ethylene intramolecular potential energy surface.

MO 5.20 Mon 17:00 C/Foyer

Temporal characterization studies of an ultrafast electron diffractometer — ●XAVIER HOLZAPFEL, CHRISTIAN GERBIG, SILVIO MORGENSTERN, MARLENE ADRIAN, ARNE SENFTLEBEN, and THOMAS BAUMERT — University of Kassel, Institute of Physics and Center of Interdisciplinary Nanostructure Science and Technology (CINSA^T), D-34132 Kassel, Germany

Time-resolved diffraction, using x-ray or electron probes, has become a promising technique to directly provide insights into dynamics at the molecular level with ultrafast precision. We study the dynamical processes in single crystalline graphite by means of ultrafast electron diffraction in order to expand the understanding of phonon generation and decay mechanisms being essential for future carbon based electronic devices. Our highly compact DC electron diffractometer is fully characterized by experiments and N-body simulations. At balanced conditions a temporal resolution of 200 fs along with high-definition diffraction is achieved for dynamical studies.

In this contribution the temporal characterization of electron pulses is discussed in dependency of different characterization methods. We use grating enhanced ponderomotive scattering and also electron pulse autocorrelation to characterize electron pulses in situ.

MO 5.21 Mon 17:00 C/Foyer

Improving the Angular Accuracy in Molecular Beam-Surface Scattering Experiments — ●PAUL SAFTIEN, BO-GAUN CHEN, and WOLFGANG CHRISTEN — Institut für Chemie, Humboldt-Universität zu Berlin, Brook-Taylor-Straße 2, 12489 Berlin, <http://clusterlab.de>

In molecular beam-surface scattering experiments a precise alignment of the incoming beam, the target surface, and the particle detector is desirable.

We present a straightforward method allowing for an accurate positioning of the solid substrate in molecular beam-surface scattering experiments such that the beam-surface-detector angle is well defined. The method is demonstrated for measurements of the angular distribution of a pulsed supersonic helium beam, scattered off a chemically inert Si(111)/SiO₂ surface. Based on a geometric model, target and detector positions are systematically varied in order to obtain a most precise surface alignment.

MO 5.22 Mon 17:00 C/Foyer

Laser-induced acoustic desorption of large molecules — ●ZHIPENG HUANG^{1,3}, DANIEL A. HORKE¹, and JOCHEN KÜPPER^{1,2,3} — ¹Center for Free-Electron Laser Science, DESY, Hamburg — ²Center for Ultrafast Imaging, University of Hamburg — ³Department of Physics, University of Hamburg

State-, conformer-, and size-selection of small neutral molecules can be achieved through the dispersion of the molecular beam with electric fields [1]. State-selected small molecules can then be well aligned and oriented by laser and static electric fields [2]. To extend these techniques to large molecules is currently limited by the ability to produce high densities of neutral large molecules in the gas-phase.

Laser-induced acoustic desorption (LIAD) is a promising technique for gentle and efficient preparation of intact neutral large molecules in vacuum. Here we demonstrate our newly set-up laser-induced acoustic desorption (LIAD) source, which is coupled to a time-of-flight mass spectrometer. We will discuss the efficiency of the source as a function of experimental parameters, such as laser pulse energy, duration and foil parameters, and discuss its potential for applications in x-ray or electron diffraction imaging.

[1] S. Y. T. van de Meerakker et al., *Chem. Rev.* **112**, 4828 (2009); Y.P. Chang et al., *Science* **342**, 98 (2013); T. Kierspel et al., *Chem. Phys. Lett.* **591**, 130 (2014); D. Horke et al., *Angew. Chem. Int. Ed.* **53**, 11965 (2014)

[2] H. Stapelfeldt et al., *Rev. Mod. Phys.* **75**, 543 (2003); S. Trippel et al., *Phys. Rev. A* **89**, 051401(R) (2014); arXiv:1409.2836

MO 5.23 Mon 17:00 C/Foyer

Investigation on Citrus Oils Using Raman Spectroscopy with Different Excitation Wavelengths — ●KATERINA KANEVCHE, RASHA HASSANEIN, BERND VON DER KAMMER, and ARNULF MATERNY — Jacobs University, Campus Ring 1, 28759 Bremen, Germany

Citrus oils are essence oils manufactured from various citrus fruits. Major constituents include *e.g.* limonene and other terpenes. Carotenoids, only found in minor quantities, present key organic pigments absorbing in the visible (VIS) range between 400 and 550 nm, thus protecting the chlorophyll deterioration due to sun-light exposure. Moreover, they act as antioxidants in the human body. Limonene and citral are mainly responsible for the odor of citrus fruits. They are used in manufacturing cosmetic products as well as food flavors, perfumes, etc. Both carotenoids and carbohydrate terpenes can be identified from their Raman spectrum. Earlier experiments have applied FT-Raman

to citrus oils. Here, we introduce Raman spectroscopy using different wavelengths in the VIS spectral range for the investigation of oils from various citrus fruits. Detailed vibrational information could be obtained much faster and resonance Raman effects could be used giving access to minor species. Chemometric analysis has been employed in order to discriminate between the different oils based on their composition. VIS Raman spectroscopy thus constitutes a fast, non-destructive analytical technique not requiring sample preparation, which would be a very attractive tool for inline monitoring of the production process and quality control of citrus oils.

MO 6: Atomic clusters (with MO)

Time: Monday 17:00–19:00

Location: C/Foyer

MO 6.1 Mon 17:00 C/Foyer

Radio-frequency buncher for core-level photoelectron spectroscopy of metal clusters at FLASH — ●FRANKLIN MARTINEZ, PATRICE OELSSNER, MICHAEL KÖTHER, JOSEF TIGGESBÄUMKER, and KARL-HEINZ MEIWES-BROER — Universität Rostock, Institut für Physik, 18055 Rostock

XUV radiation of high brilliance from the free electron laser facility FLASH (Hamburg) allows to access electronic core levels of free metallic clusters by photo-electron spectroscopy (PES). Recent experiments on lead cluster anions revealed a systematic shift of 5d and of 4f level energies as a function of cluster size. For small clusters, a variation of the electron binding energy from the metallic sphere model due to reduced core-hole screening is observed [1,2]. However, with decreasing cluster size and also with increasing photon energies, the photoionization cross sections decrease rapidly, thus limiting the photo-electron yield. To increase the target density of size-selected clusters, and hence the electron yield, a new apparatus with a linear radiofrequency ion trap is currently under construction. Perspective, the ion trap is to be combined with a radio-frequency ion buncher to increase the cluster density in the laser interaction region even further. With this setup many-electron dynamics due to x-ray photon absorption and highly correlated phenomena on ultrashort timescales in clusters will be addressed in future experiments. This contribution reports about design and simulations of the rf-buncher. The work is funded by the bmbf (FSP302), and supported by the DFG (SFB 652). [1] V. Senz et al., PRL 102, 138303 (2009). [2] J. Bahn et al., NJP 14, 075008 (2012).

MO 6.2 Mon 17:00 C/Foyer

Investigation of a ring ion trap for the production of multiply-charged cluster anions — ●STEFAN KNAUER, GERRIT MARX, and LUTZ SCHWEIKHARD — Institut für Physik, Universität Greifswald, Felix-Hausdorff-Str. 6, 17489 Greifswald

A multipole ring trap was built for systematic studies of cluster anions. The Coulomb barrier and electron binding energies of multiply-charged metal clusters are experimentally mostly uninvestigated. Because polyanionic metal-clusters do not exist in nature, they have to be produced in laboratories by cluster electron collision. This can be achieved by combinations of cluster sources and ion traps [1]. A method to investigate the Coulomb barrier is the production of negative charge states with precise electron energies. To do so, one needs a field free region for the cluster-electron interaction where, simultaneously, the cluster ions are trapped. For this purpose a multipole ring electrode trap [2] was built. The experiment consists of a magnetron sputter source [3], a quadrupole bender, the ring electrode trap and a section for time-of-flight mass spectrometry (ToF MS). The sputter source is used to produce singly-charged negative metal clusters, which are guided into the trap. Cooled cluster ions can gain multiple charge states by cluster-electron collisions. For those collisions the cluster and electrons have to interact in a field free region, which a ring-electrode trap provides. In a next step, the experiment should provide defined charge states for laser interaction experiments. The contribution will discuss the principle and design of the ring electrode trap, preliminary ion-confinement tests and corresponding mass spectra.

MO 6.3 Mon 17:00 C/Foyer

Linear Paul-trap for core-level photoelectron spectroscopy of Metal Clusters at FLASH — ●MICHAEL KÖTHER, FRANKLIN MARTINEZ, PATRICE OELSSNER, JOSEF TIGGESBÄUMKER, and KARL-

HEINZ MEIWES-BROER — Universität Rostock, Institut für Physik, 18055 Rostock

Previous photoelectron spectroscopy experiments at the free electron laser in Hamburg (FLASH) have shown distinct changes in the binding energy of lead 5d and 4f levels as a function of cluster size [1,2]. With higher photon energies available it is now possible to excite even deeper core electrons. On the other hand photoionization cross sections decrease rapidly. For compensation higher target densities are necessary and will be achieved by a new setup currently under construction. The main changes include a cryogenic, linear Paultrap and a radio frequency ion buncher. In the trap, cluster ions from a continuous source are cooled and accumulated, thus approaching a structural ground state, before pulsed extraction into the FEL interaction region. This contribution reports about simulations and first test runs of the Paultrap. The work is funded by the BMBF FSP 302, and supported by the DFG (SFB 652). [1] V. Senz et al., Phys.Rev.Lett., 102, 138303 (2009). [2] J. Bahn et al., New J. Phys., 14, 075008 (2012).

MO 6.4 Mon 17:00 C/Foyer

Electron re-localization dynamics in Xenon clusters under intense XUV pump-probe excitation — ●MATHIAS ARBEITER, CHRISTIAN PELTZ, and THOMAS FENNEL — University of Rostock, Germany

Intense and temporally structured X-ray - light fields enable the controlled generation of strongly coupled nonequilibrium cluster nanoplasma. Sub-picosecond relaxation dynamics within the cluster are revealed via the delay dependent charge states as demonstrated in recent femtosecond soft x-ray pump-probe experiments [1]. Here we report a scheme based on local electron single-particle energy spectra that enables microscopic tracing of the underlying electron-relocalization processes in molecular dynamics simulations up to the strong-coupling regime [2]. We show that recombination dynamics strongly depend on temperature and density of the system leading to a rapidly converging electron relocalization within a few picoseconds and most efficient recombination in the cluster core. A systematic pump-probe analysis reveals that electron re-localization provides a fingerprint of electron cooling and nanoplasma rarefaction through cluster expansion and yield delay-dependent ion charge states in good agreement with experiments [1]. The applied analysis is not restricted to soft x-ray excitation of clusters but essential also for the infrared regime and high harmonic light sources.

MO 6.5 Mon 17:00 C/Foyer

Microscopic description of single-shot diffractive imaging of atomic clusters — ●KATHARINA SANDER, CHRISTIAN PELTZ, and THOMAS FENNEL — Institute of Physics, University of Rostock

The availability of intense femtosecond laser pulses in the XUV and soft x-ray spectral range from free-electron lasers has made it possible to investigate the structure and dynamics of nanosystems via single-shot diffractive imaging experiments, as recently demonstrated with single clusters [1]. To study the linear light scattering in clusters theoretically we employ the discrete dipole approximation (DDA) [2]. The DDA method relies on a dyadic Greens function approach and allows to model arbitrarily shaped targets down to the atomic level. We propose a modified complex mixing scheme to increase convergence of the iterative DDA model. As a first application, we examine the possibility of imaging the recently predicted IR induced nonlinear internal plasma waves in clusters [3]. Our analysis supports that distinct features of the sub-fs dynamics can be extracted from time-resolved scattering

pictures. Second, we investigate the scattering of strongly absorbing silver clusters. A comparison with experimental results highlights the necessity to include absorption, which is neglected in the regularly applied treatment of x-ray scattering (Born approximation). Finally, we analyze the limits for the applicability of the single-frequency approximation in the modelling of scattering images.

- [1] T. Gorkhover *et al.*, Phys. Rev. Lett. **108**, 245005, (2012)
 [2] E. M. Purcell *et al.*, Astrophys. J. **186**, 705-714, (1973)
 [3] C. Varin *et al.*, Phys. Rev. Lett. **108**, 175007, (2012)

MO 6.6 Mon 17:00 C/Foyer

Time-resolved X-ray Imaging of Anisotropic Nanoplasma Expansion — ●CHRISTIAN PELTZ¹, CHARLES VARIN², THOMAS BRABEC², and THOMAS FENNEL¹ — ¹Institute of Physics, University of Rostock, Germany — ²Department of Physics and Centre for Photonics Research, University of Ottawa, Canada

We investigate the time-dependent evolution of laser-heated $R = 25$ nm solid-density hydrogen clusters via coherent diffractive imaging for an infrared pump / x-ray probe scenario. Our microscopic particle-in-cell analysis provides a full self-consistent electromagnetic description of both the droplet ionization and expansion induced by the intense few-cycle pump pulse as well as the elastic and inelastic light scattering by the x-ray probe in the expanding nano-plasma [1]. Our analysis reveals that continuous ion ablation on the cluster surface generates an anisotropic nanoplasma expansion that can be accurately described by a simple self-similar radial density profile. It's time evolution can be reconstructed precisely by fitting the time-resolved scattering images using a simplified scattering model in Born approximation. Our findings suggest, that time-resolved diffractive imaging experiments on nano-droplets will provide unprecedented insights into the physics of ion expansion and surface ablation in laser-driven plasmas [2].

- [1] C. Varin, C. Peltz, T. Brabec and T. Fennel, Phys. Rev. Lett. **108**, 175007 (2012)
 [2] C. Peltz, C. Varin, T. Brabec and T. Fennel, Phys. Rev. Lett. **113**, 133401 (2014)

MO 6.7 Mon 17:00 C/Foyer

Commissioning the Microfocus Optics for the CAMP Chamber at FLASH — ●JAN P. MÜLLER¹, BENJAMIN ERK², REBECCA BOLL², CEDRIC BOMME², EVGENY SAVELYEV², GÜNTER BRENNER², SIARHEI DZIARZHYTSKI², BARBARA KEITEL², MARION KUHLMANN², ELKE PLÖNJES², KAI TIEDKE², ROLF TREUSCH², MARIO SAUPPE¹, ANGAD SWIDERSKI², LARS GUMPRECHT³, THOMAS TILP³, FRANK

SIEWERT⁴, THOMAS ZESCHKE⁴, DANIEL ROLLES², and THOMAS MÖLLER¹ — ¹TU Berlin/ IOAP, AG Moller, 10623 Berlin — ²DESY, 22607 Hamburg — ³CFEL, 22607 Hamburg — ⁴HZB, 12489 Berlin

Free electron lasers provide a high photon flux combined with ultra-short pulse durations. A tightly focussed radiation beam enables to study atoms, molecules, clusters and particles with nonlinear effects, particularly light scattering. A focus smaller than $8 \times 9 \mu\text{m}^2$ has been reached by a newly set-up Kirkpatrick-Baez optics at the BL1 of FLASH. In combination with the permanently installed CAMP chamber [1], a multi-purpose instrument for electron and ion spectroscopy, pump-probe, and imaging experiments, it founds the base for user-experiments at high light intensities in a versatile and well-proven experimental chamber. In a first experiment very high charge states of ions from a rare gas target could be generated.

- [1] L. Strüder *et al.*, Large-format, high-speed, x-ray pnCCDs combined with electron and ion imaging spectrometers in a multipurpose chamber for experiments at 4th gen. light sources, Nucl. Instr. and Meth. in Phys. Res. A **614**, 483-496 (2010)

MO 6.8 Mon 17:00 C/Foyer

First-principles simulation of alkali-doped liquid helium at zero temperature — ●STEFAN HEMPEL, YAROSLAV LUTSYSHYN, and DIETER BAUER — Institut für Physik, Universität Rostock, 18051 Rostock, Germany

Alkali-doped helium droplets reveal unexpected physical features [1,2] and present testing grounds for first-principles quantum many-body methods [3]. In particular, multiple Mg dopants are known to form metastable structures in helium droplets [2]. We use first-principles projector Monte Carlo methods to study how the presence of the alkali atoms affects the surrounding superfluid. We will report the implications for the interpretation of the metastable structures of Mg atoms in the droplets.

- [1] M. Mudrich, F. Stienkemeier, Int. Rev. Phys. Chem. **33**, 301-339, (2014); J. Reho, U. Merker, M. R. Radcliff, K. K. Lehmann, G. Scoles, J. Chem. Phys. **112**, 8409 (2000).

- [2] A. Przystawik, S. Göde, T. Döppner, J. Tiggesbäumker, and K.-H. Meiwes-Broer, Phys. Rev. A **78**, 021202(R) (2008); S Göde, R Irsig, J Tiggesbäumker and K-H Meiwes-Broer, New J. Phys. **15**, 015026 (2013).

- [3] R. Rodríguez-Cantano, T. González-Lezana, P. Villarreal, D. López-Durán, F. A. Gianturco, G. Delgado-Barrio, Int. J. Quantum Chem. **114**, 1318 (2014); A. Nakayama, K. Yamashita, J. Chem. Phys. **114**, 780 (2001).

MO 7: Ion Traps, Molecules, Clusters, Decay and Reactions

Time: Tuesday 11:00–13:00

Location: PH/HS2

Invited Talk

MO 7.1 Tue 11:00 PH/HS2

Direct search for the neutrino mass: the KATRIN experiment — ●CHRISTIAN WEINHEIMER for the KATRIN-Collaboration — Westfälische Wilhelms-Universität Münster

Since the discovery of neutrino oscillations we know that neutrinos have non-zero masses, but the absolute neutrino mass scale is still unknown. The knowledge of the neutrino masses is very important for astrophysics and cosmology as well as for nuclear and particle physics.

With the Karlsruhe TRITium Neutrino experiment KATRIN we directly search for the neutrino mass by investigating the endpoint region of the tritium beta decay spectrum at 18.6 keV with ultra-high precision and sensitivity. This method is complementary to the search for neutrinoless double beta-decay and analyses of cosmological data.

The KATRIN experiment, which is being set up at Karlsruhe Institute for Technology, will improve the sensitivity of direct neutrino mass experiments by one order of magnitude down to $200 \text{ meV}/c^2$. The apparatus consists of a windowless gaseous tritium source, a beta electron transport and tritium elimination system based on differential and cryogenic pumping, and a doublet of electron spectrometers of MAC-E-Filter type followed by an electron detector. Its high sensitivity requires KATRIN to be technically very demanding and to drive several technologies to the extreme.

Currently the KATRIN spectrometer and detector system (SDS) is being commissioned. In this talk the status of the KATRIN experiment and the recent SDS commissioning measurements will be presented.

The work of the author is supported by BMBF Verbundforschung.

MO 7.2 Tue 11:30 PH/HS2

Auf dem Weg zum FT-ICR Nachweis mehrfach negativ geladener Clusterionen — STEFFI BANDELOW¹, FRANKLIN MARTINEZ², GERRIT MARX¹, LUTZ SCHWEIKHARD¹ und ●ALBERT VASS¹ — ¹Institut für Physik, Ernst-Moritz-Arndt Universität, 17487 Greifswald, Deutschland — ²Institut für Physik, Universität Rostock, 18055 Rostock, Deutschland

Durch die gleichzeitige Speicherung von Elektronen und Monoanionen in einer Penningfalle werden bis zu 10fach negativ geladene Metallcluster erzeugt, wobei der erreichbare Ladungszustand mit der Clustergroße steigt [1]. Die in den bisherigen Experimenten verwendete Flugzeit (ToF)-Methode ermöglicht zwar die Detektion sehr weniger Ionen, ist aber ein destruktiver Nachweis. Außerdem begrenzt das ToF-Massenaufklärungsvermögen die Identifikation der größeren Clusterpolyanionen.

In einem alternativen Ansatz soll ein Fouriertransformations-Ionenzyklotronresonanz-Nachweis (FT-ICR) implementiert werden. Hierbei werden die m/q -abhängigen Bewegungsfrequenzen der gespeicherten Ionen genutzt, deren Bildladungssignale auf den Elektroden der Penningfalle detektiert werden. Diese nichtdestruktive Methode besitzt eine größere Massenaufklärung, wenn auch bei geringerer Nachweisempfindlichkeit. Im Beitrag wird auf die Implementierung der FT-ICR-Detektion zum Nachweis mehrfach negativ geladener Cluster eingegangen und es werden erste Messergebnisse präsentiert.

- [1] F. Martinez *et al.*, Int. J. Mass Spectrom. **365-366** (2014) 266.

MO 7.3 Tue 11:45 PH/HS2

New setup to study the reactivity of metal clusters in the gas phase — ●DANIEL NEUWIRTH¹, JAN ECKHARD¹, KATHRIN LANGE¹, BRADLEY VISSER², MARTIN TSCHURL¹, and UELI HEIZ¹ — ¹Lehrstuhl für Physikalische Chemie & Catalysis Research Center, Chemistry Department, Technische Universität München, Lichtenbergstraße 4, 85748 Garching bei München, Germany — ²Paul-Scherrer Institute, 5232 Villigen PSI, Switzerland

Many properties of metal clusters differ significantly from the properties of the bulk material. For example the reactivity of such clusters depends often on charge and size. Within our group we want to investigate reactions of metal clusters with various molecules in the gas phase. Therefore clusters are produced with a laser-vaporization-cluster-source, size-selected with a quadrupole mass filter and stored within a ring electrode ion trap. The trap is filled with a buffer gas, consequently clusters and reaction products are constantly thermalized. The special geometry of the trap allows the controlled ejection of the reaction products into a reflectron mass spectrometer. As reaction time, temperature and concentration of the reactive gas can be varied, the kinetics of the reaction can be determined. First results of this experimental setup will be presented.

MO 7.4 Tue 12:00 PH/HS2

Polyanionische Metallcluster — ●STEFFI BANDELOW¹, FRANKLIN MARTINEZ², GERRIT MARX¹, LUTZ SCHWEIKHARD¹ und ALBERT VASS¹ — ¹Institut für Physik, Ernst-Moritz-Arndt Universität, 17487 Greifswald, Deutschland — ²Institut für Physik, Universität Rostock, 18055 Rostock, Deutschland

Ionenfallen haben sich als vielfältiges Instrument zur Untersuchung gespeicherter atomarer Cluster etabliert. Sie ermöglichen die Beobachtung zeitlich ausgedehnter Wechselwirkungen größenselektierter Cluster mit Elektronen, Laserstrahlung, Neutralgas oder anderen Ionen. Insbesondere eignen sie sich zur Erzeugung mehrerer negativ geladener Cluster durch Elektronenanlagerung an niedrigere Ladungszustände (z.B. Monoanionen). Die Techniken zur Polyanionenproduktion in Penningfallen und in digital betriebenen Paulfallen werden erläutert [1,2]. Für Gold- und Aluminiumcluster werden Messungen zur Auftretshäufigkeit höherer Ladungszustände als Funktion der Clustergroße und Cluster-Elektronen-Interaktionszeit diskutiert. Darüber hinaus werden Ansätze zur theoretischen Beschreibung der Stabilität polyanionischer Metallcluster bezüglich Elektronenemission vorgestellt.

[1] F. Martinez et al., *Int. J. Mass Spectrom.* 365-366 (2014) 266.

[2] S. Bandelow et al., *Int. J. Mass Spectrom.* 353 (2013) 49.

MO 7.5 Tue 12:15 PH/HS2

Cryo kinetics of size selected cobalt clusters — ●JENNIFER MOHRBACH, SEBASTIAN DILLINGER, and GEREON NIEDNER-SCHATTEBURG — Fachbereich Chemie and Forschungszentrum OPTIMAS, Technische Universität Kaiserslautern, 67663 Kaiserslautern, Germany

A customized Fourier Transform Ion Cyclotron Resonance (FT-ICR) mass spectrometer served to investigate the kinetics of nitrogen adsorption on size selected cobalt cluster cations (Co_n^+ , $9 < n < 29$) at well-defined cryo temperatures. Our setup combines a hexapole ion trap for kinetic studies with a FT-ICR cell for Infrared Multiple Photon Dissociation (IRMPD) studies and mass analysis. Both ion traps are cryogenically cooled to temperatures below 30 K. We have con-

ducted kinetic studies to determine the rates and numbers of the N_2 adsorption to the respective cobalt clusters. Furthermore we have performed IR(M)PD spectroscopy in the N-N stretching frequency range of the adsorbed nitrogen to gain insight into its binding motifs on the cluster and the structure of the cobalt clusters themselves.

MO 7.6 Tue 12:30 PH/HS2

Size-dependent gas phase reactivity of tantalum cluster cations with small alcohols — ●JAN ECKHARD¹, DANIEL NEUWIRTH¹, KATHRIN LANGE¹, BRADLEY VISSER², MARTIN TSCHURL¹, and UELI HEIZ¹ — ¹Lehrstuhl für Physikalische Chemie & Catalysis Research Center, Chemistry Department, Technische Universität München, Lichtenbergstraße 4, 85748 Garching bei München, Germany — ²Paul-Scherrer Institute, 5232 Villigen PSI, Switzerland

As the properties of metal clusters may change vastly as a function of cluster size, their study is a model approach to find and tune catalysts for use in specific reactions. The detailed investigation of metal clusters is facilitated in the gas phase. As a result, we found a strong size dependence for the reactivity of tantalum cluster cations with small alcohol molecules. The clusters were produced in the gas phase by laser vaporization; various alcohols (methanol, ethanol, n-propanol and 2-propanol) were consecutively added to the cluster beam in a pulsed jet and allowed to react to an extent of conversion of approximately 50%. The charged reaction products were subsequently measured using time-of-flight mass spectrometry. Two distinct reaction pathways were observed, involving complete dehydrogenation or OH abstraction from the alcohol molecule. The relative total reaction yield was found to not vary significantly within the cluster size regime studied. The branching ratios for the reaction demonstrated a cluster-size dependence, with a minimum of OH abstraction occurring for a cluster size of 7 atoms.

MO 7.7 Tue 12:45 PH/HS2

Slow molecular beams of biochromophores via laser induced acoustic desorption — ●UGUR SEZER¹, LISA WÖRNER¹, CHRISTOPH GÖTZ², ALPASHA VAZIRI², and MARKUS ARNDT¹ — ¹University of Vienna, Faculty of Physics, VCQ and QuNaBioS, Boltzmanngasse 5, 1090 Vienna, Austria — ²University of Vienna, Max F. Perutz Laboratories; Research Institute of Molecular Pathology; QuNaBioS, Doktor-Bohr-Gasse 7, 1030 Vienna, Austria.

A beam of intact, neutral, and slow molecules is an essential criterion for experiments in physical chemistry and quantum optics, such as deflectometry and matter-wave interferometry[1]. Different molecular beam methods have been developed over recent years, among them thermal beams of functionalized molecules[2], free laser desorption[3] or supersonic expansion of laser desorbed molecules[4].

In this work we show that beams of intact, neutral, biologically relevant chromophores, such as chlorophyll a and hemin can be launched in high vacuum with mean velocities as low as 45 m/s with minimal fragmentation. The molecules are volatilized via laser-induced acoustic desorption[5], photoionized with lasers light at 157 nm or 266 nm, and detected in time-of-flight mass spectrometry. We present mass spectra, desorption and photoionization efficiencies as well as velocity distributions and discuss possible applications.

[1] K. Hornberger et al. *Rev. Mod. Phys.* 2012, 84. [2] S. Eibenberger et al. *Phys. Chem. Chem. Phys.* 2013, 15. [3] P. Schmid et al. *J. Am. Soc. Mass. Spectrom.* 2013, 24. [4] M.-H. Ha-Thi et al. *Phys. Chem. Chem. Phys.* 2010, 12. [5] A.V. Zinoviev et al. *Anal. Chem.* 2007, 79.

MO 8: Theory: Quantum Chemistry

Time: Tuesday 11:00–13:00

Location: PH/HS1

Invited Talk

MO 8.1 Tue 11:00 PH/HS1

Novel computational approaches to molecular electronic-structure theory — ●WIM KLOPPER — Karlsruhe Institute of Technology (KIT), Institute of Physical Chemistry, Fritz-Haber-Weg 2, 76131 Karlsruhe, Germany — Karlsruhe Institute of Technology (KIT), Institute of Nanotechnology, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

The talk will give an overview of some recent progress made (in the Karlsruhe research group) in the development of computational approaches to molecular electronic-structure theory. These approaches comprise methods that employ explicitly correlated wave functions on

the one hand and methods based on a quasirelativistic two-component framework on the other. Concerning explicitly correlated wave functions, we have recently implemented a direct ring-coupled-cluster-doubles (drCCD) method that employs such functions and which yields density-functional electron-correlation energies in the random-phase approximation in the limit of a complete one-electron basis set. Concerning quasirelativistic two-component methods, we have recently implemented a corresponding linear-response, approximate coupled-cluster method (in the CC2 approximation) for the treatment of electronically excited states. These methods have been implemented in the TURBOMOLE program package and examples of their application will be given. The talk will also provide examples of recent applications of

other computational methods available in this program package.

MO 8.2 Tue 11:30 PH/HS1

MC-Potfit: Transforming high-dimensional potential energy surfaces into a sum-of-products form using Monte-Carlo methods — ●MARKUS SCHRÖDER and HANS-DIETER MEYER — Physikalisch-Chemisches Institut, Universität Heidelberg, Im Neuenheimer Feld 229, 69120 Heidelberg

We present a Monte-Carlo variant of the well known Potfit algorithm [Jäckle *et al.*, J. Chem. Phys. 104, 7974 (1996)] to transform potential energy surfaces into a sum-of-products form. This transformation leads to an enormous reduction of data and in particular to a representation of the potential which is suitable for calculations with the Heidelberg multi-configuration time-dependent Hartree method. The modified Potfit variant uses Monte-Carlo integration techniques and can therefore be used to tackle larger problems than the original Potfit. Furthermore, inclusion of weight functions to emphasize important regions of the potential is straight forward. We present example calculations and discuss benefits and limitations of the algorithm.

MO 8.3 Tue 11:45 PH/HS1

A relativistic time-dependent density functional study of the excited states of the group 12 dimers (Zn2-Cn2). — ●OSSAMA KULLIE — Institut für Physik, Universität Kassel

We use the (relativistic) time-dependent density functional (TDDFT) to study the ground-state as well as the excited states corresponding to the atomic asymptotes ($ns^2 + nsnp$), ($ns^2 + ns(n+1)s$) and ($ns^2 + ns(n+1)p$), $n=4-7$, for these dimers (Zn2-Cn2) [1]. We analyze the spectrum obtained from all-electron calculations performed with the relativistic Dirac-Coulomb and relativistic spinfree Hamiltonian as implemented in Dirac-Package. A comparison with the literature is given as far as available. A detailed analysis of the spectrum of the dimers is given, including a comparative analysis especially for the relativistic effects, the spin-orbit interaction, and the performance of some well-known density functionals. [1] O. Kullie. J. Chem. Phys. **140**, 024304 (2014). O. Kullie Chem. Phys. **415**, 112 (2013). O. Kullie. (open access) J. At. Mol. Opt. Phys. **2012**, 361947 (2012).

MO 8.4 Tue 12:00 PH/HS1

Multi-Reference Theoretical Approach to Photoelectron Spectroscopy — ●GILBERT GRELL, SERGEY I. BOKAREV, and OLIVER KÜHN — Institut für Physik, Universität Rostock, Universitätsplatz 3, D-18055 Rostock, Germany

The L-edge X-ray photoelectron and Auger spectroscopy is a powerful tool for investigating the local electronic structure of transition metal compounds in condensed and gaseous phases. The assignment and analysis of the results obtained for transition metal ions in solution [1] requires high-quality theoretical methods.

Here, we utilize the multi-reference Restricted Active Space SCF (RASSCF) method together with state interaction (RASSI) for spin-orbit coupling [2], implemented in the MOLCAS program package to obtain high quality wave functions. On this basis, XPS matrix elements are calculated using a Dyson orbital approach [3]. Applications will be presented for aqueous transition metal ions surrounded by the first solvation shell.

1. R. Seidel *et al.* J. Am. Chem. Soc. 134, 1600 (2012), S. Thürmer *et al.* J. Am. Chem. Soc. 133, 12528 (2011)
2. P. A. Malmquist *et al.* Chem. Phys Lett. 357, 230 (2002)
3. C. Melania Oana *et al.* J. Chem. Phys. 127, 234106 (2007)

MO 8.5 Tue 12:15 PH/HS1

Electronic structure calculations of multiple core hole states in molecules — YAJIANG HAO^{1,2}, ●LUDGER INHETER², SANG-KIL SON², and ROBIN SANTRA^{2,3} — ¹CFEL, Desy, Hamburg — ²USTB, Beijing, China — ³Fachbereich Physik, Universität Hamburg

Newly available x-ray light sources such as X-ray Free Electron Lasers

allow one to study highly excited electronic states with one or several core vacancies. These states may appear with significant probability if a sample is exposed to highly intense x-ray radiation and, they may, thus, crucially determine the evolution of radiation damage[1]. Further, spectroscopy of multiple core hole states is of great relevance, because the associated strong chemical shifts reveal detailed information on the surrounding chemical environment[2,3].

For the theoretical modelling of these states a relative large basis set is required to capture the strong electronic relaxation effects upon core ionization. We present a new scheme for the electronic structure calculation of these states based on basis functions obtained by previous atomic Hartree-Fock-Slater calculations[3]. Results are shown for all combinations of core vacancies in the carbon monoxide molecule. By using basis functions adapted to the respective core vacancy states, we show that the number of the basis functions can be reduced while achieving results of similar quality. This reduction makes calculations of multiple core hole states also in larger molecules feasible.

- [1] Young *et al.* Nature 466, 56 (2010) [2] Cederbaum *et al.* JCP 85, 6513 (1986) [3] Berrah *et al.* PNAS 108, 16912 (2011) [4] Son *et al.* PRA 83, 033402 (2011)

MO 8.6 Tue 12:30 PH/HS1

Population dynamics, decoherence and wave packet splitting: The essential features of non-adiabatic process from a novel trajectory-based quantum-classical method — ●SEUNG KYU MIN, FEDERICA AGOSTINI, and E. K. U. GROSS — Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, D-06120 Halle, Germany

We present a novel quantum-classical algorithm to non-adiabatic dynamics that is deduced from the coupled electronic and nuclear equations in turn derived in the framework of the exact factorization[1] of the electron-nuclear wave function. The aim is to devise a trajectory-based procedure which is free of the shortcomings from the conventional approaches and therefore able to capture the basic physics of non-adiabatic process. The theoretical derivation will be supported by numerical results that are compared to quantum mechanical calculations[2].

- [1] A. Abedi, N.T. Maitra, and E.K.U.Gross, Phys.Rev.Lett. 105, 123002 (2010); J. Chem. Phys. 137, 22A530 (2012). [2] S.K. Min, F. Agostini, and E.K.U. Gross, in preparation.

MO 8.7 Tue 12:45 PH/HS1

Using ICD for structural analysis of clusters: A case study on NeAr clusters — ●ELKE FASSHAUER¹, MARKO FÖRSTEL², SEBASTIAN PALLMANN³, MARKUS PERNPÖNTNER³, and UWE HERGENHAHN⁴ — ¹CTCC, Department of Chemistry, University of Tromsø, N-9037 Tromsø, Norway — ²University of Hawai'i at Manoa, 96816 HI Honolulu, USA — ³Theoretische Chemie, Universität Heidelberg, 69120 Heidelberg, Germany — ⁴Max Planck Institute for Plasma Physics, 17491 Greifswald, Germany

We present a method to utilize Interatomic Coulombic Decay (ICD) to retrieve information about mean geometric structures of heteronuclear clusters. It is based on observation and modelling of competing ICD channels, which involve the same initial vacancy, but energetically different final states with vacancies in different components of the cluster. Using binary rare gas clusters of Ne and Ar as an example, we measure the relative intensity of ICD into $(\text{Ne}^+)_2$ and Ne^+Ar^+ final states with spectroscopically well separated ICD peaks. We compare in detail the experimental ratios of the Ne-Ne and Ne-Ar ICD contributions and their positions and widths to values calculated for a diverse set of possible structures. We conclude that NeAr clusters exhibit a core-shell structure with an argon core surrounded by complete neon shells and, possibly, further incomplete shell of neon atoms for the experimental conditions investigated. Our analysis allows to differentiate between clusters of similar size and stoichiometric Ar content, but different internal structure. We find evidence for ICD of Ne $2s^{-1}$, producing Ar^+ vacancies in the second coordination shell of the initial site.

MO 9: Femtosecond Spectroscopy 2

Time: Tuesday 14:30–16:30

Location: PH/HS1

Invited Talk

MO 9.1 Tue 14:30 PH/HS1

Control and Spectroscopy of Chiral Systems in the Condensed Phase — ●TOBIAS BRIXNER — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

Chirality is a fundamental structural property arising from symmetry considerations: A chiral object cannot be superimposed with its mirror image. In this presentation, progress will be shown toward chirally selective control and time-resolved chiral spectroscopy of molecules in the condensed phase. For this purpose, a variety of fundamental and practical issues have to be addressed. Solutions to some of the problems will be discussed. As a means to introduce chirality via light in the most flexible fashion, we have developed vector-field shaping with independent ultrafast control over amplitude, phase, and polarization of an ultrashort pulse as a function of time. Another necessary ingredient is a detection method that provides chiral sensitivity. We have constructed a highly sensitive polarimeter and used it together with accumulative spectroscopy to measure the optical rotation change upon a chirality-modifying photochemical reaction. Thus we achieved all-optical discrimination between racemic and achiral molecular solutions. A second option for chiral detection is to measure photoinduced changes in circular dichroism (CD). Using a new setup for creating “light-pulse enantiomers”, we have developed broadband time-resolved CD spectroscopy with shot-to-shot white-light detection. As an example, we investigated oxygen release in hemoglobin.

MO 9.2 Tue 15:00 PH/HS1

Improving Fluorescence Kerr Gating — ●RAMONA MUNDT, GERALD RYSECK, and PETER GILCH — HHU Düsseldorf, Germany

With Kerr gating complete fluorescence spectra as a function of time may be recorded in the femto- to picosecond regime[1]. This advantage over fluorescence up-conversion comes at the expense of an increased background. The background is caused by fluorescence leaking through the polarizers and third harmonic generation of the gate pulses. In the contribution it will be shown that the implementation of reference diodes and a correction procedure greatly increases the data quality.

[1] B. Schmidt et al., Appl. Phys. B, 2003, 76/8, 809-814

MO 9.3 Tue 15:15 PH/HS1

Ultrafast dissociation of molecular oxygen excited at 162 nm wavelength — ●THOMAS GEBERT, DIMITRIOS ROMPOTIS, MAREK WIELAND, FAWAD KARIMI, ARMIN AZIMA, and MARKUS DRESCHER — Institut für Experimentalphysik, Universität Hamburg, Deutschland

Ultrafast dissociation of excited gas-phase oxygen molecules is studied through vacuum-ultraviolet two photon ionization in an interferometric VUV pump-probe experiment. Using powerful fifth harmonic radiation from a Ti:Sa laser with up to 1 uJ pulse energy and a pulse duration of 18 femtosecond at 162 nanometre wavelength a precision of below 2 femtosecond is achieved.

MO 9.4 Tue 15:30 PH/HS1

Jumping and Diffusion of Excitons: Förster transfer drives annihilation in an organic system — ●FRANZISKA FENNEL and STEFAN LOCHBRUNNER — Institut für Physik, Universitätsplatz 3, 18055 Rostock

In many organic materials absorption of light leads to the formation of mobile electronic excitations, i.e. Frenkel excitons. At high excitation densities they can interact with each other resulting in an accelerated decay of the exciton density due to exciton-exciton-annihilation. We investigate the underlying mechanisms and the subsequent steps of annihilation in a disordered organic model system by ultrafast absorption spectroscopy. The time dependent exciton density can be described by two annihilation pathways, the direct energy transfer between two excited molecules and diffusive motion towards a second exciton preceding the annihilation event. It is found that both pathways can be quantitatively understood by applying Förster energy transfer theory to describe the diffusion of the excitons as well as the annihilation step itself. To this end previous formulations of Förster theory are extended to account for the inhomogeneous distribution of the S_0 - S_1 transition energies resulting in an effective diffusion constant. Our

model system consists of dye molecules embedded in a PMMA matrix. This model system allows to tune the exciton diffusion constant via the chromophore concentration [1] and therefore one annihilation pathway can be emphasized with respect to the other.

[1] F. Fennel, S. Lochbrunner, *Phys. Chem. Chem. Phys.* **13**, 3527 (2011)

MO 9.5 Tue 15:45 PH/HS1

Tracking energy flow through the intact photosynthetic apparatus of green sulfur bacteria *in situ*. — ●JAKUB DOSTÁL¹, JAKUB PŠENČÍK², and DONATAS ZIGMANTAS³ — ¹Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany — ²Faculty of Mathematic and Physics, Charles University in Prague, Ke Karlovu 3, 121 16 Prague, Czech Republic — ³Department of Chemical Physics, Lund University, P.O.Box 124, 221 00 Lund, Sweden

In order to utilize the energy of solar radiation the photosynthetic organisms developed various types of photosynthetic apparatuses. The photosynthetic apparatus of green sulfur bacterium *Chlorobaculum tepidum* consists of chlorosome - a massive light-harvesting antenna, FMO protein - the excitation energy conduit, and the reaction center. All the constituting complexes are clearly distinguishable in the absorption spectrum of the suspension of intact bacterial cells taken at low temperatures (77 K). This opens a possibility to study the light-harvesting processes by means of ultrafast time-resolved spectroscopy *in situ*. In this work we have applied coherent two-dimensional electronic spectroscopy to resolve the excitation energy flow through the entire photosynthetic apparatus.

MO 9.6 Tue 16:00 PH/HS1

Identification of an Ultrafast Triplet Transition Discovered by Pump-Depletion-Probe Experiments — ●JULIA HERZ¹, FABIAN PAULUS², TIAGO BUCKUP¹, UWE BUNZ², and MARCUS MOTZKUS¹ — ¹Physikalisch-Chemisches Institut — ²Organisch-Chemisches Institut, Ruprecht-Karls-Universität, D-69120 Heidelberg, Germany

Pump-depletion-probe experiments were carried out in order to disentangle the excited state dynamics of TIPS-pentacene. In particular the singlet fission process, in which an excited molecule reacts with a neighbor in its ground state producing two excited triplet species in an overall spin-conserved process, is important. The formed triplet state shows two transitions, one in the visible (T1->T3) and one in the NIR spectral region (T1->T2). Measurements in these two spectral ranges can provide insight into the interplay of the triplet manifold and help to unravel additional singlet fission channels. Applying a depletion pulse resonant with the triplet absorption in the visible leads to a loss of signal in the NIR, however, the evolution of the NIR signal does not follow the dynamics observed in the visible. Our results are explained by an ultrafast relaxation channel (ca. 90 fs) between the triplet states (T3->T2). A rate model simulation of the depletion effect supports this finding and gives further evidence, within our experimental time resolution, that both triplet transitions in the NIR and VIS probe the same triplet state (T1).

MO 9.7 Tue 16:15 PH/HS1

Collinear two-dimensional spectroscopy via fluorescence detection with rapid phase cycling — ●SIMON DRAEGER¹, SEBASTIAN RÖDING¹, ANDREAS STEINBACHER¹, PATRICK NÜRNBERGER^{1,2}, and TOBIAS BRIXNER¹ — ¹Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg — ²Physikalische Chemie II, Ruhr-Universität Bochum, Universitätsstraße 150, 44780 Bochum

We present a novel all-collinear setup to perform pulse-shaper-assisted two-dimensional electronic spectroscopy with fluorescence detection. The acousto-optical pulse shaper (Dazzler, Fastlite) allows the variation of the interpulse delays and their relative phases with 1 kHz rate, enabling a rapid scan and shot-to-shot phase cycling. For a four-pulse sequence with variable delay times τ , T and t , the application of phase cycling allows to obtain different nonlinear contributions (e.g. rephasing and non-rephasing photon echo) in one single measurement process. Common laser dyes are used as benchmark molecules to evaluate the setup.

MO 10: Experimental Techniques

Time: Tuesday 14:30–16:15

Location: PH/SR106

MO 10.1 Tue 14:30 PH/SR106

Luminescence Characterization of Mass-Selected Electro-sprayed Ions Embedded in Rare-Gas Matrices — ●BASTIAN KERN¹, JEAN-FRANCOIS GREISCH^{1,2}, DMITRY STRELNIKOV¹, ARTUR BÖTTCHER¹, PATRICK WEIS¹, DETLEF SCHOSS^{1,2}, BERHARD SCHÄFER², MARIO RUBEN^{2,3}, and MANFRED M. KAPPES^{1,2} — ¹Physikalische Chemie Mikroskopischer Systeme, Karlsruhe Institute of Technology, Fritz-Haber Weg 2, 76131 Karlsruhe, Germany — ²Institute of Nanotechnology, Karlsruhe Institute of Technology, Hermann-von-Helmholtz Platz 1, 76344 Eggenstein-Leopoldshafen, Germany — ³Institute of Inorganic Chemistry, Karlsruhe Institute of Technology, Engesserstr. 15, 76131 Karlsruhe, Germany

The combination of electrospray ionization (ESI), laser-induced luminescence, and matrix isolation is demonstrated for the first time using lanthanide diketonate ions. The accumulation of mass-selected ions over several hours into a cryogenic rare-gas matrix yields material amounts large enough for sensitive measurements on elusive species whose properties are typically masked in standard condensed-phase measurements. With the additional advantage of measurements at 5K, spectra were obtained which display sharp emission lines. Comparison of matrix laser induced luminescence measurements with those on trapped ions in the gas phase show a remarkable agreement, i. e. the vibronic bands are close to identical. This suggests that the neon matrix used induces only negligible geometrical and electronical perturbations to the species studied.

MO 10.2 Tue 14:45 PH/SR106

Polarisation Infrared Spectroscopy on Oriented Substrates (PIROS) - A case study on Phenazine — MICHAELA BRAUN, GERNOT ENGLER, KATHARINA HUNGER, ●ALEXANDER WOHLERT, KARL KLEINERMANN, and MICHAEL SCHMITT — Universität, Düsseldorf, Germany

Vibrationally induced changes of the molecular dipole moment give rise to different band types in infrared spectroscopy. According to the projection of the molecule's normal modes onto the inertial axes of the molecule these bands can be classified as a, b or c types. In case of molecules with C_{2v}, D₂- or D_{2h}-symmetry the inertial axes and the components of the dipole moment are parallel to each other and therefore the molecules normal modes can easily be classified. In crystals or molecules oriented in films on surfaces, the absorption of polarized IR light depends on the orientation of the molecules with respect to the surface and the plane of polarization of the light. Since the dipole moment changes have a well-defined orientation with respect to the molecular frame, defined by the main inertial axes, the orientation of the molecules on a surface can be determined from the dependence of the IR intensities using polarized IR light, while rotating the sample along the axis of the He-Ne-Laser-beam. To test this method we chose the phenazine molecule since it has D_{2h} symmetry.

MO 10.3 Tue 15:00 PH/SR106

Non-destructive State Detection and Identification of Molecular Ions — ●AMY GARDNER, WILLIAM GROOM, and MATTHIAS KELLER — Ion Trap Cavity QED and Molecular physics (ITCM) group, University of Sussex, UK

The nature of ion traps allow for extremely well localised atomic and sympathetically cooled molecular species; leading to a variety of applications - most notably cold chemistry, testing fundamental theories, searching for changes in fundamental constants and, potentially, the development of methods for quantum computing. Prerequisite for these applications is the cooling of the molecule's motion and its non-invasive identification. Furthermore, the internal quantum state of the molecule needs to be prepared and, at readout, non-destructively detected.

While blackbody assisted laser cooling was recently demonstrated, the non-destructive state detection of trapped molecules is still beyond current experiments. Employing state selective laser induced dipole forces we aim to detect the internal state of molecular ions by mapping the state information onto the ions motion.

We can also identify different ionic species within a coulomb crystal by measuring the average charge-to-mass ratio of trapped ions with high precision. This is a tool that can be used to investigate chemical reactions between neutral molecules/atoms and trapped molecular

ions. The same means can also be achieved by using only laser forces.

MO 10.4 Tue 15:15 PH/SR106

Characterization of an electron gun for diffraction experiments on controlled gas-phase molecules — ●NELE L. M. MÜLLER¹, SEBASTIAN TRIPPEL¹, TERENCE G. MULLINS¹, and JOCHEN KÜPPER^{1,2,3} — ¹Center for Free-Electron Laser Science, DESY, Hamburg — ²The Hamburg Center for Ultrafast Imaging, Hamburg — ³Department of Physics, University of Hamburg

The aim of the presented work is to investigate the structure and dynamics of molecules in the gas-phase by electron diffraction experiments. Controlling the molecules' state and spatial orientation increases the amount of information contained in electron diffraction patterns. The contribution presents our newly set-up electron gun that will be combined with an existing controlled-molecules apparatus. In the controlled-molecules setup gas-phase molecules are state-selected by means of electric deflection and then laser-aligned to serve as a well-defined sample [1]. The developed DC electron gun can produce up to 10 million electrons per pulse and uses an electro-static lens for focusing. The focusing electrodes are arranged in a configuration similar to a velocity map imaging spectrometer. Initially, they can be used to measure the spatial and velocity distribution of the electron pulse at the cathode. In combination with electron trajectory simulations this allows for further characterization of the electron beam, as for example the determination of pulse duration and coherence length. Electron diffraction data from solid state and gaseous samples will be presented.

[1]Trippel et al., *Mol. Phys.* **111**, 1738-1743 (2013)

MO 10.5 Tue 15:30 PH/SR106

Microsolvation and coordination changes in a dinuclear iron-palladium complex in isolation — ●MAXIMILIAN GAFFGA, JOHANNES LANG, ISABEL MUNSTEIN, WERNER R. THIEL, and GEREON NIEDNER-SCHATTEBURG — Fachbereich Chemie und Forschungszentrum OPTIMAS Technische Universität Kaiserslautern, Germany

We have applied a combination of mass spectrometric and spectroscopic techniques to determine the composition and structure of isolated cationic dinuclear transition metal complexes in the gas phase. The ions are stored in a Paul trap after creation by electrospray ionization (ESI) for collision induced dissociation (CID) and Infrared Multi Photon Dissociation (IRMPD) investigations. Solvent residues after the ESI process serve as a model system for microsolvation. Fragmentation reactions of these complexes are investigated in detail by CID experiments. These studies lead to surprising information about the fragmentation behavior of the complexes. The combination of DFT calculations and CID results allow for a better understanding of these fragmentation pathways. These investigations exhibit reliable structure proposals of prominent product ions. Assignment of vibrational bands and identification of the complex coordination pattern arise from comparison of IRMPD spectra in the range of 1200-4000 cm⁻¹ to calculated spectra (B3LYP/cc-pvDZ,ECP).

MO 10.6 Tue 15:45 PH/SR106

Structural Studies of Molecular Clusters by Broadband Rotational Spectroscopy — ●CRISTOBAL PEREZ and MELANIE SCHNELL — Max-Planck Institute for the Structure and Dynamics of Cold and Controlled Molecules, Hamburg, Germany

Recent advances in high-speed digital electronics have been used to achieve unprecedented speed and sensitivity in broadband rotational spectroscopy. Such high-speed digitizers allow deep time-domain signal averaging. This new level of sensitivity allows the study of weakly bonded molecular clusters of which several examples will be shown to highlight the performance of this spectrometer.

MO 10.7 Tue 16:00 PH/SR106

Gasphase Spectroscopy of small Carbon-Bearing Molecules — ●DANIEL WITSCH, STEVEN INGUNZA, VOLKER LUTTER, GUIDO FUCHS, and THOMAS GIESEN — University of Kassel - Institute of Physics, Germany, Heinrich-Platt-Str 40, 34132 Kassel

Asymptotic giant branch (AGB) stars show a huge variety of carbon-bearing molecules. Thus, laboratory based investigations of these clusters are important to enable astrophysical detections of further species.

We present an experimental setup to study gasphase IR-spectra of these molecules at low temperatures.

For this purpose a laser ablation source is used to produce a carbon containing plasma. Helium carries the ablated material through a reaction channel, where the desired molecules are formed. Subsequent adiabatic expansion cools the molecules to a few 10K of rotational

temperature.

This technique combined with quantum cascade lasers allows for high resolution IR-spectroscopy of carbon-bearing molecules. Especially the finger-print region from 2 to 12 microns is of great interest since many rovibrational transitions can be detected here.

MO 11: Posters 2: Novelties in Molecular Physics

Time: Tuesday 17:00–19:00

Location: C/Foyer

MO 11.1 Tue 17:00 C/Foyer

Circular dichroism in photoionization of chiral systems by intense laser pulses — ●ANTON N ARTEMYEV¹, ANNE D MÜLLER¹, DAVID HOCHSTUHL², and PHILIPP V DEMEKHIN¹ — ¹Institut für Physik, Universität Kassel, Heinrich-Plett-Str. 40, 34132 Kassel — ²Institut für Theoretische Physik und Astrophysik, 24098 Kiel

It is well known that chiral molecules interact in different ways with left and right circular polarized light. This phenomenon is known as circular dichroism. Here, we systematically investigate circular dichroism in the angular-resolved photoionization and above threshold ionization spectra of model chiral systems. To this end, we numerically solve the time-dependent Schrödinger equation for the single-active-electron wave-packet in a chiral pseudo-potential in the presence of intense circularly polarized laser pulses. The results, obtained in different model potentials for fixed-in-space and randomly oriented systems, are reported.

MO 11.2 Tue 17:00 C/Foyer

Solvent Dependence of Photochemical Reactions of Molecules based on Pyranine — ●CHRISTIAN SPIES¹, BJÖRN FINKLER², and GREGOR JUNG² — ¹Physical Chemistry II, Ruhr-University Bochum, Bochum, Germany — ²Biophysical Chemistry, Saarland University, Saarbrücken, Germany

The transfer of a proton to a base is one of the most fundamental chemical reactions. Especially, photoexcitation of aromatic alcohols, leading to an enhanced acidity, served as paradigm for this kind of reaction. One of the most widely used photoacids is hydroxypyrene-trisulfonate (HPTS) and its even more acidic sulfonamide derivative (HPTA).[1] Recently, we synthesized a series of strong photoacids based on HPTS, with high photostability and pKa* values ranging from -0.7 to -4.[2] A charge transfer was identified as the most distinct feature for the strong solvatochromism and photoacidity of these molecules.[3] The excited-state proton transfer rate (kPT) of these photoacids in different solvents was measured by time-resolved spectroscopy.[4] In this contribution, we also transfer our results to molecules with an asymmetric substitution pattern and the new diazonium derivative of HPTS.

[1] D. Spry, M. Fayer, J. Chem. Phys., 127 (2007) 204501. [2] B. Finkler, C. Spies, M. Vester, F. Walte, K. Omlor, I. Riemann, M. Zimmer, F. Stracke, M. Gerhards, G. Jung, Photochem. Photobiol. Sci. 13 (2014), 548. [3] C. Spies, B. Finkler, N. Acar, G. Jung, Phys. Chem. Chem. Phys., 15 (2013) 19893. [4] C. Spies, S. Shomer, B. Finkler, D. Pines, E. Pines, D. Huppert, G. Jung, Phys. Chem. Chem. Phys., 16 (2014) 9104.

MO 11.3 Tue 17:00 C/Foyer

Double Valence Ionization of Propadiene — ●MIRIAM WELLER^{1,2}, MARKUS SCHÖFFLER¹, BISHWANATH GAIRE², MARTIN RICHTER¹, ALEXANDER HARTUNG¹, AVERELL GATTON^{2,3}, SEBASTIAN ALBRECHT^{1,2}, JAMES SARTOR³, BEN BERRY⁴, MARKO HÄRTELT⁵, JOSHUA WILLIAMS¹, TILL JAHNKE¹, ALLEN LANDERS³, REINHARD DÖRNER¹, and THORSTEN WEBER² — ¹IKF, Goethe-Universität Frankfurt am Main, Max-von-Laue-Str. 1, 60438 Frankfurt, Germany — ²LBNL, 1 Cyclotron Road, Berkeley, CA 94720, USA — ³Auburn University, Auburn, AL 36849-5311, USA — ⁴Kansas State University, 116 Cardwell Hall, Manhattan, KS 66506, USA — ⁵NRC/uOttawa, 100 Sussex Drive, Ottawa ON K1A 0R6, Canada

Due to their structure, cumulenes of configurations as $H_2C_nH_2$ ($n \geq 2$) are of high importance in a broad field of chemical processes like combustion, chemistry of atmosphere and interstellar media and also in more technical applications like nanomechanics and nanoelectronics.

We studied the breakup of propadiene ($H_2C_3H_2$) after double ionization induced by 40 eV and 53 eV synchrotron radiation. A COLTRIMS reaction-microscope was used to measure the momenta of both the re-

coil ions and the two ejected electrons in coincidence. We were able to observe several breakup channels ($H^+/C_3H_3^+$; $H_2^+/C_3H_2^+$; H_3^+/C_3H^+ and $CH_2^+/C_2H_2^+$), different excited electronic states of the dication and angular distributions of the reaction products. Depending on the photon energy, different double ionization processes take place. At higher energies, a sequential channel opens which we assume to be delayed autoionization like previously observed in smaller molecules.

MO 11.4 Tue 17:00 C/Foyer

Ultrafast photodynamics of a trinuclear palladium complex studied by femtosecond time-resolved transient UV/Vis and mid-IR spectroscopy — ●FABIAN RUPP¹, ZIMMER MANUEL¹, YVONNE SCHMITT¹, KATHARINA CHEVALIER¹, DIMITRI IMANBAEW¹, YEVGENIY NOSENKO¹, CHRISTOPH RIEHN¹, FRANK BREHER², MARKUS GERHARDS¹, WIM KLOPPER², and ROLF DILLER¹ — ¹TU Kaiserslautern, 67663 Kaiserslautern — ²Karlsruhe Institute of Technology, 76131 Karlsruhe

Multinuclear transition metal complexes with their promising cooperative effects are very attractive for new electronic devices or chemical catalysis. Here we investigated the photophysical properties of a trinuclear Pd₃ complex [Pd₃{Si(mt^{Me})₃}₂][1] solved in DMSO-d₆. After electronic excitation at 330 nm the system undergoes a photocycle with ultrafast formation of a long lived luminescent triplet state ³A₁ ($\tau_{fluo} = 1.4 - 1.7 \mu s$, $\lambda_{fluo} = 675 \text{ nm}$).[2] The ultrafast formation of the emissive electronic state is monitored by fs UV/Vis spectroscopy (380 fs) in solution and photofragmentation (200 fs) for the ionic complex in gas phase, whereas vibrational cooling ($\tau_{VC} = 7.8 \text{ ps}$) is clearly observed via fs mid-IR spectroscopy in solution. Additional step-scan FTIR measurements exhibit no further structural changes on longer time scales (ns to μs). The experimental vibrational spectra are in very good agreement with TD-DFT calculations.

[1] F. Armbruster et al., Chem. Commun., 2011, **47**, 221

[2] Y. Schmitt et al., PCCP, 2014, **16**, 8332

MO 11.5 Tue 17:00 C/Foyer

Laser control of exciton localization in perturbed molecular aggregates — ●JOHANNES WEHNER, CHRISTOPH BRÜNING, JULIAN HAUSNER, and VOLKER ENGEL — Institut für Physikalische und Theoretische Chemie, Emil-Fischer-Str. 42, Universität Würzburg, 97074 Würzburg, Germany

A site specific perturbation of a photo-excited molecular aggregate can lead to a localization of the excitonic energy on the site where the perturbation acts. We investigate such localization dynamics in linear and cyclic aggregates. Vibronic eigenstates or wave packets in the excited state manifold can be prepared by using different excitation pulses. This selective excitation has a significant influence on the localization of excitons.

MO 11.6 Tue 17:00 C/Foyer

Towards Time-Resolved Structural Imaging of Transition State Dynamics — ●KATRIN REININGER and JOCHEN MIKOSCH — Max-Born-Institut, Berlin

The transition state marks a short time span during a chemical reaction in which molecular structures exist that are neither the reagents nor the reaction products. This is the time when old bonds are broken and new bonds are formed. Due to the difficulty to access the very transient transition state structures in an experiment there are a lot of open questions surrounding transition state dynamics.

We are developing a novel probe that images, one molecule at a time, the time-dependent spatial structure of individual transition states as they evolve on a femto- to picosecond time scale. For this we combine two modern techniques of molecular physics: (i) Reaction precursors are prepared as small ion-dipole complexes of molecular ions

with defined and tunable internal temperature. These serve as starting point for inducing transition state dynamics by photodissociation or photodetachment of a chromophore. (ii) Coulomb Explosion Imaging, induced by extremely short and intense infrared laser pulses as a function of time-delay, and its full coincidence momentum imaging will then be used to follow the dynamics and ultimately to reconstruct the evolving spatial molecular geometry.

It is anticipated that our studies will shed new light on the defining, but also most elusive part of chemical reaction dynamics.

MO 11.7 Tue 17:00 C/Foyer

Excited states dynamics of trinuclear lanthanide complexes [Ln(III)Mn(II)₂-L] in gas phase and solution — ●FLORIAN LIEDY¹, FABIAN RUPP¹, FLORIAN BÄPPLER¹, SEBASTIAN KRUPPA¹, DIMITRI IMANBAEW¹, YEVGENIY NOSENKO¹, PETER W. ROESKY², CHRISTOPH RIEHN¹, and ROLF DILLER¹ — ¹TU Kaiserslautern, 67663 Kaiserslautern — ²Karlsruhe Institute of Technology, 76131 Karlsruhe

Metallic coordination compounds containing lanthanides have attained enormous interest due to their single-molecular-magnet and unique luminescent properties. They may serve for applications in quantum computers, high density data storage or OLEDs. We employed femtosecond time-resolved transient UV/Vis- and photofragmentation spectroscopy to elucidate the excited states dynamics and luminescent behavior of three trinuclear [Ln(III)Mn(II)₂-L] [1] complexes containing Dy(III), Eu(III) or Lu(III); L=ligand.

After electronic excitation at 360 nm in solution we observe for all three derivatives the formation of the excited S₁^{*} state within the experimental response time (< 150 fs) and a subsequent relaxation to the electronic ground state within 10–11 ps. The kinetic analysis yielded three kinetic components of $\tau_1 = 0.4$ ps, $\tau_2 = 1.7 - 2.1$ ps, $\tau_3 = 10 - 11$ ps that are tentatively assigned to stimulated emission and non-radiative decays of the S₁^{*} state (τ_1) and non-radiative decays of an intra-ligand-charge-transfer state (τ_2) and a triplet ligand state (τ_3). Our photofragmentation experiments revealed also three kinetic components on the same timescale for the Eu(III) derivate.

[1] Bhunia et al., Inorg. Chem., 2012, **51**, 9589

MO 11.8 Tue 17:00 C/Foyer

Multimodal Time-Resolved Spectroscopy: Combining Transient Absorption and Fifth-order Spectroscopies — ●TAKESHI MIKI, MARCUS MOTZKUS, and TIAGO BUCKUP — Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, D-69120 Heidelberg, Germany

Ultrafast spectroscopy is able to address many different molecular degrees of freedom by applying several kinds of time-resolved spectroscopic methods (TRSM). In spite of the success of each TRSM to unravel specific parts of the molecular dynamics (intra- and intermolecular, electronic or structural), the long-standing goal of correlating such aspects with each other, and, therefore, combining them under one general molecular model is still a major challenge in spectroscopy. In this work we demonstrate the advantages of performing several time-resolved techniques like transient absorption and pump-DFWM (transient grating and photon echo) in one single experimental setup under similar experimental parameters. We develop a fitting a model and show for two prototype organic molecules in solution how transient absorption data can be combined with time-resolved vibrational pump-transient grating and pump-photon echo. Such a multimodal time resolved spectroscopy allows for unambiguously determination of the amplitude and phase of all major oscillatory contributions due to intra- as well as intermolecular dynamics, in spite of the background-free (homodyne) detection geometry.

MO 11.9 Tue 17:00 C/Foyer

Molecular Frame Photoelectron Angular Distributions in CF₃I Molecules — ●FELIX BRAUSSE, ARNAUD ROUZÉE, and MARC VRAKKING — Max-Born-Institut für nichtlineare Optik, Berlin

Over the last decade, the emergence of X-ray free-electron lasers (FELs) and high-order harmonic generation (HHG) XUV-sources has enabled the development of diffractive methods for imaging time-resolved molecular dynamics. One of the main driving forces behind the development of the FEL is the possibility to perform x-ray diffractive imaging of larger molecules; alternatively, diffractive information can as well be encoded onto photoelectrons that are generated by the ionisation of the molecules with an ultrashort XUV or X-ray pulse. As the photoelectron is emitted, it scatters off the molecule's multi-centre potential, leading to a diffraction pattern in the final electron momentum distribution.

Here, we present the first step towards the diffractive imaging of the dissociation dynamics of CF₃I molecules, induced by a 266 nm pump excitation: we observed the photoelectron angular distributions (PADs) of field-free aligned CF₃I molecules. They were ionised by a monochromatic XUV pulse that was obtained from HHG with a 400 nm driving field. Also, we compare the measured PADs to scattering simulations employing the Schwinger variational principle.

MO 11.10 Tue 17:00 C/Foyer

Sub-cycle control of electron dynamics in atoms and molecules — ●HENDRIKE BRAUN¹, TIM BAYER², MATTHIAS WOLLENHAUPT², and THOMAS BAUMERT¹ — ¹Universität Kassel, Institut für Physik und CINSaT, D-34132 Kassel, Germany — ²Carl von Ossietzky Universität Oldenburg, Institut für Physik, 26129 Oldenburg, Germany

The electron dynamics in atoms as well as the concerted electron-nuclear dynamics in molecules can be controlled by the resonant AC stark effect [1]. The Selective Population Of Dressed States (SPODS) allows us to manipulate the interaction energy of the quantum system and the driving laser pulse to steer the electronic population into a predefined target channel. To this end we tailor the optical phase of femtosecond laserpulses to the induced dipolemoment in the quantum system and thereby control the intricate interplay of the driving electric field and the induced electronic coherence [2,3]. The necessary sub-cycle precision in shaping the laserpulses to control the electron dynamics on their inherent timescale of atto- to few femtoseconds is highlighted as well as the theoretical and experimental efficiency of the control scheme. Furthermore we explore the possibility of adiabatic control scenarios in systems with coupled degrees of freedom [4].

[1] T. Bayer *et al.*, invited article Adv. Chem. Physics, submitted

[2] H. Braun *et al.*, J. Phys. B **47**, 124015 (2014)

[3] T. Bayer *et al.*, Phys. Rev. Lett. **110**, 123003 (2013)

[4] J. Schneider *et al.*, Phys. Chem. Chem. Phys. **13**, 8733 (2011)

MO 11.11 Tue 17:00 C/Foyer

Structural investigations on an isolated depsipeptide by combined IR/UV laser spectroscopy in a molecular beam — ●DOMINIC BERNHARD, ANKE STAMM, and MARKUS GERHARDS — Physikalische Chemie, TU Kaiserslautern, Erwin-Schrödinger-Straße 52, 67663 Kaiserslautern

Depsipeptides are often found to be natural antibiotics, such as the cyclic depsipeptides beauvericin and valinomycin. For a better understanding of their antibiotic effect on a molecular level, knowledge on the structure of the isolated molecules is of importance. As a first model system we chose the linear depsipeptide cyclohexylcarbonyl-glycine-lactate-2-anisidine (CyCO-Gly-Lac-NH-PhOMe) whose structural investigation should give basic insights into conformational preferences of isolated depsipeptides. For that reason combined double and triple resonance IR/UV laser spectroscopic methods were applied in a molecular beam experiment. In combination with DFT calculations the mass- and isomerselective experimental methods are suitable tools to get information on conformational preferences of the isolated depsipeptides in the electronic ground state (S₀). The recorded spectra revealed the existence of more than one isomer in the molecular beam. A comparison of the IR spectra with DFT calculations allowed structural assignments; the influence of dispersion interactions was taken into account. The most stable structure was found to be a strongly folded one involving C-H... π interactions.

MO 11.12 Tue 17:00 C/Foyer

A versatile neutral-ion collision setup for the CSR — ●FLORIAN GRUSSIE, MANFRED GRIESER, AODH P. O'CONNOR, and HOLGER KRECKEL — Max-Planck-Institut für Kernphysik, Heidelberg

Ion-neutral reactions are pre-eminent processes in the chemical network of interstellar clouds. With typical cloud temperatures ranging from 10 to 100 K, neutral-neutral reactions tend to be energetically quenched. Anion-cation reactions, although often barrier-less, are limited due to the relatively low abundance of anions in interstellar clouds. With approximately 180 cosmic molecules detected to date, two-body neutral-ion collisions are prevalent in the formation of complex molecules. Despite their importance, most ion-neutral reactions have no experimental thermal rate coefficient data at astrophysically relevant conditions.

To study these processes, we are currently developing an apparatus to merge cooled stored ions (~ 10 K) with a well-defined neutral atomic beam. To this end, a negative ion beam with a kinetic energy of up to 300 keV, is crossed with a continuous wave high-power (2 kW) diode

laser, operating at 808 nm. Neutral particles are created by photodetachment and merged with stored ions in a straight section of the Cryogenic Storage Ring (CSR) at a tuneable center of mass collision energy. The CSR, located at the Max Planck Institute for Nuclear Physics in Heidelberg, provides a cold environment (~ 10 K) with extremely low residual gas pressure. Measurement of the particle fluxes, beam overlap and the production rate of daughter products enable determination of absolute reaction rate coefficients.

MO 11.13 Tue 17:00 C/Foyer

Metal cluster-diamondoid hybrids studied with ion yield spectroscopy — ●TOBIAS ZIMMERMANN¹, ANDRE KNECHT¹, ROBERT RICHTER¹, ANDREA MERLI¹, KONSTANTIN HIRSCH², MERLE RÖHR³, JENS PETERSEN³, ROLAND MITRIC³, TOBIAS LAU², THOMAS MÖLLER¹, and TORBJÖRN RANDEL¹ — ¹Technische Universität Berlin — ²Helmholtz-Zentrum für Materialien und Energie, Berlin — ³Julius-Maximilians-Universität Würzburg

Diamondoids, a class of sp^3 -hybridized, hydrogen passivated carbon nanostructures, show shape and size dependent optical properties. They are interesting as light emitting materials due to their UV fluorescence properties. However, the fluorescence quantum yield of diamondoid compounds has been shown to be low.

Plasmon resonance effects are known to enhance the absorption and emission in nanometer-sized noble metal particles. Combinations of diamondoids with subnanometer metal clusters are promising candidates for the study of such fundamental coupling mechanisms, in a size regime where every atom counts, that might potentially increase the fluorescence quantum yield by orders of magnitudes.

Hybrids of diamondoids and noble metal clusters were synthesized and studied. Their absorption in a linear ion trap was recorded with ion yield spectroscopy both in the UV and the optical domain. We present the initial results of this study.

MO 11.14 Tue 17:00 C/Foyer

Analysing destruction channels of interstellar hydrocarbon anions with a 22-pol ion trap — ●ERIC ENDRES¹, OLGA LAKHMANSKAYA¹, DANIEL HAUSER¹, STEFAN HUBER², THORSTEN BEST¹, SUNIL KUMAR³, MICHAEL PROBST¹, and ROLAND WESTER¹ — ¹Institute for Ion Physics and Applied Physics, University of Innsbruck, 6020 Innsbruck, Austria — ²now at: Department of Chemistry TU München, 85747 Garching, Germany — ³now at Max Planck Institut für Nuclear Physics, 69029 Heidelberg, Germany

Ion-molecule reactions are considered to play a key role in the formation of complex molecules in the interstellar medium. The recently detected interstellar carbon chain anions [1,2] are probably adding new pathways to create large molecules. To gain insight into the presence and influence of these interstellar anions, a detailed analysis of the possible destruction channels is indispensable. A cryogenic 22-pol radio frequency ion trap is a ideal tool to observe rare reactions at low temperature.

Here, we report on upper limits to the reaction rates for C_n^- and C_nH^- ($n = 2, 4, 6$) with buffer gas temperatures of H_2 at 12 and 300 K. The experimental results are discussed in light of quantum chemical simulation and implemented in a gas-phase astrochemical[3]. An outlook towards possible chain elongation reaction will be shown.

[1] M.C. McCarthy et al., Ap.J. (2006); [2] J. Cernicharo et al., A&A (2007); [3] E. Endres et al., J. Phys. Chem. A (2014)

MO 11.15 Tue 17:00 C/Foyer

Laser cooling and trapping of decelerated SrF molecules — ●CORINE MEINEMA, JOOST VAN DEN BERG, SREEKANTH MATHAVAN, ARTEM ZAPARA, LORENZ WILLMANN, KLAUS JUNGSMANN, and STEVEN HOEKSTRA — University of Groningen, Netherlands

We are preparing a parity violation measurement in heavy diatomic molecules. Therefore we need ultracold (SrF) molecules in a well-defined quantum state. Molecules are created in a supersonic expansion and decelerated by a traveling-wave Stark decelerator. The decelerated molecules have a temperature of 150 mK and laser cooling will reduce this further. For most types of the molecules, laser cooling is not possible due to the many long-living rotational and vibrational states. However, SrF has an almost closed rovibrational transition, where laser cooling is possible. We designed an extension of the decelerator to give access to laser beams. On the poster we also show a way to increase the number of decelerated molecules by optical pumping.

MO 11.16 Tue 17:00 C/Foyer

Quasi-1d Collisions of $^{87}Rb_2$ molecules — ●BJÖRN DREWS,

MARKUS DEISS, and JOHANNES HECKER DENSCHLAG — Institut of Quantum Matter

We observe Rubidium molecules in the Feshbach and $^3\Sigma_u$ ($v=0$) state, colliding in a strongly anisotropic, quasi-1d potential. All interactions take place in an optical lattice in the ultracold regime. The filling in each 1d trap is on average only 3-4 molecules over a length of about $80 \mu m$. This leads to complex dynamics in the time evolution of the system. A simple, intuitive model is devised to simulate this behavior and to extract the corresponding decay coefficients.

MO 11.17 Tue 17:00 C/Foyer

Spectroscopic investigation of molecular processes in liquid hydrogen isotopologues — ●SEBASTIAN MIRZ and ROBIN GRÖSSLE — Karlsruhe Institute of Technology (KIT), Institute of Technical Physics (ITEP), Tritium Laboratory Karlsruhe (TLK)

Due to their simple molecular structure the six hydrogen isotopologues Q_2 (H_2 , HD, D_2 , HT, DT, T_2) provide a unique opportunity to study molecular processes on a quantum mechanically describable level. The single bonded Q_2 can be excited to rotational or vibrational states by the interaction with light. Therefore spectroscopic techniques as Raman and IR absorption spectroscopy are ideal methods for their investigation. A fundamental access to the molecular properties like energy levels can be gained through molecular constants which can be extracted out of accurate Raman line positions of all hydrogen isotopologues. A method for their measurement in the gas phase with the aim of producing a complete set of molecular constants will be illustrated. In the liquid phase where intermolecular interactions are much more common than in the gas phase IR absorption spectroscopy is used as an experimental technique. Results of a study observing interactions between two molecules, so called dimers, and results of a calibration of the infrared absorption against the isotopologic concentration for the inactive hydrogen isotopologues H_2 , HD, D_2 will be presented. Finally an outlook to a tritium compatible spectroscopy experiment at the Tritium Laboratory Karlsruhe for temperatures ~ 20 K will be given.

MO 11.18 Tue 17:00 C/Foyer

Investigation of Organic Complexes in Helium Nanodroplets — ●ALEXANDER RUF, MARKUS MÜLLER, SHARAREH IZADNIA, AARON LA FORGE, and FRANK STIENKEMEIER — Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str.3, 79104 Freiburg

Organic molecules used as either organic semiconductors or as dyes in organic solar cells have gained high interest due to their optoelectronic properties. To reveal the electronic structure of these molecules, we use Helium Nanodroplet Isolation Spectroscopy, a well-established method to characterize both single molecules and molecular complexes inside a cold (370mK), weakly-interacting environment.

Typically, for radiative complexes or single molecules, Laser Induced Fluorescence (LIF) excitation and emission spectra is used to give spectroscopic insight into the vibrational structure of the electronic ground state and the first electronically-excited state. However, the excited states of charge-transfer-complexes (CTC), which are of particular interest for electro-optical applications, are not accessible with these techniques since their Charge-transfer-states are excited indirectly through a multi-level process and primarily de-excite nonradiatively. Therefore, entirely new experimental approaches are needed and currently being developed in our group.

We present LIF absorption and fluorescence emission spectra of various organic molecules and complexes attached to Helium Nanodroplets. Furthermore, we outline the experimental techniques designed to gain information on the non-radiative energy-transfer-processes in CTCs.

MO 11.19 Tue 17:00 C/Foyer

Numerical quantization of a semi-classical model for non-rigid asymmetric rotors — ●HANNO SCHMIEDT¹, PER JENSEN², and STEPHAN SCHLEMMER¹ — ¹I. Physikalisches Institut, Universität zu Köln — ²FB-9 - Physikalisches Chemie, Bergische Universität Wuppertal

We present a numerical semiclassical method to determine the rotational energy levels of non-rigid asymmetric rotors. Using a Green's function based approach to the rotational problem in the Born-Oppenheimer approximation we are able to predict the energies and the symmetries of the rotational wavefunction. Using this needs calculations of periodic orbits in phase space which is performed by using the molecular symmetry group elements. Also tunneling paths can be

determined by symmetry operations and are included in the energy calculation. As one possible application we will use the TROVE program to calculate the rotational energy surface and determine the energy levels by this semi-classical method, which reduces the needed calculation time by factors. As a real example we use a non-rigid asymmetric rotor, namely SO_2 , for which the centrifugal constants were previously fitted to experimental data, which were recorded up to transitions including $J = 80$ levels. We show that the semiclassical predictions and the respective quantum model energies are in good agreement.

MO 11.20 Tue 17:00 C/Foyer

Gas Phase Studies of Chiral Carbonyls with Circular Dichroism - Resonance-enhanced Multiphoton Ionization (CD-REMPI) — •JÖRN LEPELMEIER, KATHARINA TITZE, ARAS KARTOUZIAN, ULRICH HEIZ, and ULRICH BOESL — Chair of Physical Chemistry & Catalysis Research Center, Technische Universität München, Germany

The Circular Dichroism - Resonance-enhanced Multiphoton Ionization (CD-REMPI) technique combines the enantiosensitivity of CD spectroscopy with the wavelength selectivity of REMPI by using circularly instead of linearly polarized light. In addition the usage of a Time Of Flight - Mass Spectrometer (TOF-MS) provides a mass separation of the ionized sample molecules. Thus, CD-REMPI enables a three dimensional discrimination for chiral molecules in the gas phase and reduces the sample preparation to a minimum. Therefore, it affords for example ideal attributes for the stereoselective catalysis which needs a fast and sensitive detection method for product molecules in vacuum directly after their reaction.

Our contribution should demonstrate the functionality of the CD-REMPI method with measurements of the asymmetry factor g of chiral carbonyls under varied conditions due to effusive or supersonic gas inlet and one- or two-color ionization [1][2].

[1] U. Boesl, A. Bornschlegel, C. Logé and K. Titze, *Analytical and Bioanalytical Chemistry* 405 (2013) 6913-6924

[2] K. Titze, T. Zollitsch, U. Heiz and U. Boesl, *ChemPhysChem* 15 (2014) 2762-2767

MO 11.21 Tue 17:00 C/Foyer

Optical guiding of single particles for diffractive imaging with x-ray free electron lasers — •SALAH AWEL^{1,2}, RICK KIRIAN¹, NIKO ECKERSKORN³, ANDREI RODE³, JOCHEN KÜPPER^{1,2}, and HENRY CHAPMAN^{1,2} — ¹Center for Free-Electron Laser Science, DESY, Hamburg — ²Center for Ultrafast Imaging, University of Hamburg Department of Physics — ³Australian National University

The availability of brief, intense, and coherent x-ray pulses produced by x-ray free-electron lasers (XFELs) has created the potential for major advancements in macromolecular structure determination. Serial femtosecond crystallography (SFX) is among the most successful paradigms to emerge. It consists of directing a stream of randomly oriented protein microcrystals, cell, virus or molecules across the focus of

the XFEL beam. However, delivering single particles to a sub-micron x-ray focus remains a considerable challenge. Current sample delivery efficiency for single-particle imaging based on aerodynamic lens systems are on the order of 10^{-7} on average, which renders experiments infeasible for samples that cannot be obtained in high abundance. In order to confront this challenge, we are developing techniques for manipulating aerosolized nanoparticles with specially shaped laser illumination [1]. Our experiments are presently aimed at transversely confining streams of particles as they exit an aerosol injector, with a counter-propagating “hollow” quasi-Bessel beam. The experiment exploits radiation pressure and thermal (photophoretic) forces arising from the interaction of the particles with surrounding gas.

[1] *Opt. Exp.* **21**, 30492-30499 (2013)

MO 11.22 Tue 17:00 C/Foyer

A chirped pulse spectrometer for supersonic jet applications — •JOHANNA CHANTZOS, DORIS HERBERTH, and THOMAS GIESEN — Universität Kassel, Kassel 34132, Deutschland

We present an experimental setup for a broadband chirped pulse Fourier transform spectrometer. This technique enables fast scan absorption spectroscopy of transient molecules with astrophysical relevance.

An arbitrary waveform generator (AWG) with a 400 MSamples/s sample rate generates chirped pulses with a linear frequency sweep in the MHz regime and a pulse duration of a few microseconds. These pulses are up-converted in the microwave frequency range with a 10 GHz Synthesizer and subsequently pass through a multiplier that increases the pulse bandwidth without changing the pulse duration. The pulses are coupled into a gas cell either for absorption or emission spectroscopy of a free induction decay signal (FID). A high-speed oscilloscope provides the frequency domain spectrum by fast Fourier transformation of the signal.

Species of relevance are carbon chain molecules and small metal-containing refractory molecules. Recent results and development are presented.

MO 11.23 Tue 17:00 C/Foyer

Pure state vs. density matrix approaches for non-Markovian open quantum systems — •PAN-PAN ZHANG¹, DANIEL SUESS¹, WALTER T. STRUNZ², and ALEXANDER EISFELD¹ — ¹MPIPKS Dresden — ²TU Dresden

To efficiently treat non-Markovian open quantum systems is a challenging task. One often used approach, denoted as HEOM [1], is using a hierarchy of coupled operator equations.

In this contribution we compare the recently developed hierarchy of pure states (HOPS) [2], which is a stochastic method, with the corresponding hierarchy of operators. We find in particular that in general HOPS requires much less numerical resources than HEOM.

[1] Y. Tanimura; *J Phys Soc Japan* 75 082001

[2] D. Suess et al; *Phys. Rev. Lett.* 113, 150403

MO 12: Photochemistry and Catalysis

Time: Wednesday 11:00–12:45

Location: PH/HS1

Invited Talk

MO 12.1 Wed 11:00 PH/HS1

Generating high-valent iron with light. Photochemical dynamics — •PETER VÖHRINGER — Institute for Physical and Theoretical Chemistry, University of Bonn, Wegelerstrasse 12, 53115 Bonn, Germany

The most abundant oxidation states of iron are the ferrous and ferric states, +II and +III, respectively. High-valent iron compounds contain Fe centers at the extraordinary oxidation states, +IV, +V, and +VI. Such species are of paramount importance for the catalysis of a number of biochemically or technologically relevant molecular transformations. Particularly reactive are high-valent iron species that feature a terminal iron-nitrogen bond, so called nitridoiron compounds, and in which the metal is embedded in a fourfold-symmetrical coordination geometry like in heme proteins. Their isolation has not been accomplished to date, but very few non-heme model systems have been prepared by photochemical means and cryo-trapped in low-temperature solid matrices. Very recently, we have been able to temporally trap such elusive octahedral nitridoiron species even in room temperature liquid solution, i.e. under biochemically and technologically relevant condi-

tions, and to even allow for a preliminary study of their reactivity. To this end, we conducted various time-resolved infrared spectroscopies in combination with laser flash photolysis on time scales ranging from a few seconds all the way down to a few hundred femtoseconds. We will review our current state of understanding of the molecular-level mechanisms that are involved in the photochemical route to high-valent iron species as seen through these time-resolved IR methods.

MO 12.2 Wed 11:30 PH/HS1

Hydrogen Abstractions by Triplet Excited Pyrimidinones — •CHRISTIAN TORRES ZIEGENBEIN¹, MATHIAS MICHEEL², GERALD RYSECK¹, and PETER GILCH¹ — ¹HHU Düsseldorf, Universitätsstr. 1, 40225 Düsseldorf, Germany — ²IPHT-Jena, Albert-Einstein-Straße 9, 07745 Jena, Germany

Pyrimidinones are moieties of the (6-4) photolesions of DNA. Their lowest energy absorption peaks are located at longer wavelengths than those of DNA bases. Under solar irradiation this results in high excitation probabilities and can lead to secondary DNA photo lesions [1]. Pyrimidinones may exhibit high quantum yields for triplet excitation. For example 1-methy-2(1H)-pyrimidinone (1MP) features a yield of

~0.5 (50%) [2]. In how far this kind of excitation contributes to the secondary photochemistry of DNA is the topic of this presentation. By means of steady state and nanosecond spectroscopy photoreactions of 1MP and quenchers bearing a CH₂-O- moieties have been studied. The experiments show that triplet excited 1 MP abstracts hydrogen atoms from these quenchers. In particular, it could also abstract hydrogen atoms from deoxyribose pointing to the biological relevance of the process.

[1] K. Haiser, B. P. Fingerhut, K. Heil, A. Glas, T. T. Herzog, B. M. Pilles, W. J. Schreier, W. Zinth, R. de Vivie-Riedle, T. Carell, *Angew Chem Int Edit* 2012, 51, 408-411.

[2] G. Ryseck, T. Schmierer, K. Haiser, W. Schreier, W. Zinth, P. Gilch, *ChemPhysChem* 2011, 12, 1880-1888.

MO 12.3 Wed 11:45 PH/HS1

Time-Resolved Step-Scan FTIR Investigations on Multimetallic Transition Metal Complexes in Solution and in the Solid State — ●MANUEL ZIMMER¹, FABIAN RUPP¹, DANIEL VOLZ², WIM KLOPPER², ROLF DILLER¹, STEFAN BRÄSE², FRANK BREHER², and MARKUS GERHARDS¹ — ¹TU Kaiserslautern, 67663 Kaiserslautern — ²Karlsruhe Institute of Technology, 76131 Karlsruhe

Time-resolved (TR) infrared experiments enable the investigation of chemical reactions, photochemical/-physical processes and their kinetic traces. With the step-scan technique we are able to identify electronically excited states and excited state structures by comparison with theoretical results from quantum chemical calculations. Our focus lies on cooperative effects in multimetallic transition metal complexes with 2 to 4 metal centers. Here we present the first TR step-scan FTIR measurements on a trimetallic Pd complex which has been demonstrated to be a potential catalyst for coupling reactions. The complex was investigated in solution (DMSO-d₆) in the absence of air. We could determine the emissive electronic state (³A) and the structural arrangement of the complex in the excited state by comparing the excited state IR spectra with (TD-)DFT calculations. The excited state lifetime of the emissive state, which was previously obtained by fluorescence lifetime measurements is confirmed. Furthermore we present results on different dimetallic copper complexes (differing in their ligand systems) in a KBr matrix. We show the capabilities of step-scan measurements in a KBr matrix, a method that is extremely useful for complexes which cannot be investigated in solution.

MO 12.4 Wed 12:00 PH/HS1

Light-Driven Electron and Energy Transfer in a Photocatalytic Model System — ●ALEKSEJ FRIEDRICH¹, ESTEBAN MEJÍA², SHU-PING LUO², HENRIK JUNGE², MATTHIAS BELLER², and STEFAN LOCHBRUNNER¹ — ¹Institute of Physics, University of Rostock, 18051 Rostock, Germany — ²Leibniz-Institut für Katalyse e.V. an der Universität Rostock, Albert-Einstein-Str. 29a, 18059 Rostock, Germany

A promising route to provide environmentally friendly energy is the generation of solar fuels by photocatalysis. We investigate a hydrogen evolving homogeneous photocatalytic model system consisting of a non-noble metal-photosensitizer (PS), an iron-catalyst, and triethylamine (TEA) as a sacrificial reductant.[1,2] So far little is known, about the fundamental reaction steps and possible loss channels. Here we study the intermolecular electron and energy transfer by time resolved luminescence and transient absorption spectroscopy on the nanosecond timescale. It is found that 20 vol% of the sacrificial reductant reduces the luminescence lifetime of the copper-PS in acetonitrile moderately from 280 ns to 210 ns. Contrary, the iron-catalyst quenches the lifetime more efficiently to 110 ns. Long living products of the

quenching events are observed by the transient absorption measurements. To identify the products and to determine the transfer yield control experiments with the strong electron acceptor methyl viologen are performed. By comparison the electron transfer efficiency from the PS to the catalyst is determined to 4%.

Literature: [1] S. Luo et al., *Angew. Chem.* **125**, 437-441 (2012). [2] E. Mejía et al., *Chem. Eur. J.* **19**, 15972-15978 (2013).

MO 12.5 Wed 12:15 PH/HS1

Ultrafast Time-Resolved Spectroscopy of New Reversible Photoswitchable Diarylethene Derivates — ●TIAGO BUCKUP¹, SVEN MEHLHOSE¹, CHRISTOPHER SARTER², ANDRES JÄSCHKE², HANS-ROBERT VOLPP¹, and MARCUS MOTZKUS¹ — ¹Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg. — ²Institut für Pharmazie und Molekulare Biotechnologie, Ruprecht-Karls-Universität Heidelberg, D-69120 Heidelberg, Germany.

Diarylethenes (DE) are an important class of compounds with promising applications due to their photochromatic behavior. Recently, photoswitchable DEs were combined with the structural features and molecular recognition properties of nucleic acids to design new photochromic nucleosides [1]. In this work, we investigate the ultrafast dynamics of the ring-opening photo-reaction of several DE derivatives with ultrashort excitation (<20 fs) in transient absorption. We observe a very fast excited state ballistic deactivation of the Franck Condon region towards the conical intersection (CI) within the first 300 fs. The ring-opening reaction takes place within 1.6-5.5 ps, depending on the DE derivative. The branching ratio at the CI can be estimated by the incomplete recovery of the bleach signal of the closed-form absorption between 450-500 nm. The quantum yield for the ring-opening photo-reaction of such DE derivatives is significantly enhanced (over 70% efficiencies) by specific thiophene substitutions. A global target analysis (GTA) of transient absorption data further depicts a simple kinetic model starting with a sequential reaction followed by a branching reaction at the CI. [1] Singer, et al, *JACS* 132 (2010) 8372.

MO 12.6 Wed 12:30 PH/HS1

Alkali effect on bimetallic hydroamination catalysts the gas-phase — ●JOHANNES LANG, PATRICK DI MARTINO-FUMO, MERVE CAYIR, WERNER R. THIEL, and GEREON NIEDNER-SCHATTEBURG — Fachbereich Chemie und Forschungszentrum OPTIMAS, Technische Universität Kaiserslautern, Germany

Electrospray ionization (ESI) in combination with tandem mass spectrometry is an established tool to investigate transition metal complexes[1] as well as alkali ion adducts[2] under isolated conditions in the gasphase. We investigated bimetallic hydroamination catalysts via ESI-MS of their alkali adducts in a Paul type ion trap. Using a multi-methods approach we characterized the structural changes of the catalysts upon coordination of the alkali ion as well as gradual changes of the structure and fragmentation behavior. We record Infrared Multiple Photon Dissociation (IRMPD) spectra and conduct density functional theory (B3LYP/cc pVDZ, RSC ECP) calculations. Collision Induced Dissociation (CID) studies reveal a gradual change of the fragmentation behavior in dependence of the alkali ion size. This is well understood under consideration of calculated binding energies. The alkali ion size plays a crucial role in the stabilization of the fragments, which leads to a change of the fragmentation behavior.

1. Nosenko, Y., et al., *Physical Chemistry Chemical Physics*, 2013, 15(21): p. 8171-8178.

2. Citir, M., et al., *The Journal of Physical Chemistry A*, 2012, 116(6): p. 1532-1541.

MO 13: Collisions & Energy Transfer

Time: Wednesday 11:00–13:00

Location: PH/SR106

Invited Talk

MO 13.1 Wed 11:00 PH/SR106

Cryo-stored ion beams for studying neutral production in molecular fragmentation — ●ANDREAS WOLF — Max-Planck-Institut für Kernphysik, Heidelberg

Reactive and unimolecular fragmentation are powerful tools for probing molecular composition, structure, potential surfaces and internal dynamics. Energetic ion beams are unique in offering access to the neutral fragments, which can be efficiently detected and kinematically analyzed in coincidence measurements. In the cryogenic ion

storage ring CSR [1], molecular ion beams accelerated by up to 300 kV circulate in a low-temperature and low-pressure environment suppressing collisional and radiative background interactions, while the molecules are excited or fragmented by velocity-tuned merged particle beams (electrons or atoms) or by lasers. The CSR energy is particularly suited for calorimetric single-particle fragment detection [2]. Studies on the neutral fragmentation, ranging to direct fragment-mass detection and kinetic energy release measurements, will become feasible for a wide range of complex singly-charged species, including (de-)protonated compounds, radical ions and ionic clusters. We will

present the experimental method and discuss the options for complex molecules, considering in particular the interface to ion beam generation and to fragmentation detection methods. – See presentations at this meeting by [1] R. von Hahn et al. and [2] L. Gamer et al. in the session on Ion Storage Rings, Fachverband Massenspektrometrie.

MO 13.2 Wed 11:30 PH/SR106

Imaging the influence of vibrational excitation in ion-molecule reactions — ●MARTIN STEI¹, EDUARDO CARRASCOSA¹, ALEXANDER DÖRFLER², MARTIN KAINZ¹, JENNIFER MEYER¹, and ROLAND WESTER¹ — ¹Institute for Ion Physics and Applied Physics, University of Innsbruck, 6020 Innsbruck, Austria — ²now at: Department of Chemistry, University of Basel, 4056 Basel, Switzerland

We study the dynamics of ion-molecule reactions by kinematically complete velocity map imaging in a crossed-beam setup [1]. One major focus of our research is reactions of halide anions with methylhalides, a model system for nucleophilic substitution (S_N2) reactions [2]. An open question is how vibrational excitation of the reactant molecules would influence these reaction.

Here, we report on reactions of F^- and Cl^- with vibrationally excited CH_3I in the CH_3 symmetric stretch (ν_1) mode. This excitation is provided by rotationally selective excitation of the $^0R(3)$ line with a narrowband dye laser and probed by REMPI.

For F^- we find an enhancement of the rate of the proton transfer channel for the excited vibrational state. We will discuss the implications of our findings for the S_N2 channel.

[1] R. Wester, Phys. Chem. Chem. Phys. 16, 396 (2014) [2] J. Xie, R. Otto, J. Mikosch, J. Zhang, R. Wester, and W. L. Hase, Acct. Chem. Res. 47, 2960 (2014)

MO 13.3 Wed 11:45 PH/SR106

Dissociative Recombination measurements of SH^+ — ●ARNO BECKER¹, CHRISTIAN DOMESLE¹, WOLF GEPPERT², CLAUDE KRANTZ¹, OLDŘICH NOVOTNÝ^{1,3}, DANIEL SAVIN³, DIRK SCHWALM^{1,4}, BIAN YANG⁵, and ANDREAS WOLF¹ — ¹Max-Planck-Institut für Kernphysik, Heidelberg — ²Stockholm University, Stockholm, Sweden — ³Columbia Astrophysics Laboratory, New York, USA — ⁴Weizmann Institute of Science, Rehovot, Israel — ⁵Chinese Academy of Sciences, Lanzhou, PRC

Astrophysicists observe trace molecules to investigate the properties of interstellar medium. SH^+ is believed to be a very efficient probe for energetic interstellar environments, such as shocked gas. To interpret the observations, however, the models need reliable experimental data on dissociative recombination (DR) of SH^+ .

To this end we have experimentally investigated DR of SH^+ at the Test Storage Ring (TSR) of the Max Planck Institute for Nuclear Physics in Heidelberg, Germany. An SH^+ beam was merged with a cold electron beam produced by a photo-cathode. Utilizing an energy sensitive Si detector, recombination rate coefficients were determined for collision energies ranging from sub-meV up to 6 eV, covering kinetic temperatures down to 10 K. Moreover, we have determined branching ratios for various product excitation states utilizing a position sensitive microchannel plate detector. Here, we have employed a novel approach requiring detection of only one fragmentation partner. The method will be a valuable tool for analyzing imaging data of the heavier molecules to be stored in the upcoming Cryogenic Storage Ring (CSR).

MO 13.4 Wed 12:00 PH/SR106

Collective excitation in energetic proton collision with naphthalene — ●PREETI M MISHRA^{1,2}, JYOTI RAJPUT³, C P SAFVAN⁴, SARITA VIG¹, and UMESH KADHANE¹ — ¹Indian Institute of Space Science and Technology, Trivandrum-695547, India — ²Max-Planck-Institut für Kernphysik, Saupfercheckweg 1, 69117 Heidelberg, Germany — ³University of Delhi, Delhi-110 007, India — ⁴Inter-University Accelerator Centre, Aruna Asaf Ali Marg, New Delhi-110 067, India

The structural and dynamical study for Polycyclic aromatic hydrocarbons (PAHs) is important in astrophysics as well as in medical science. Due to delocalized electrons, PAHs show collective excitation characterized by large oscillator strength which are difficult to isolate from other physical processes due to broader energy deposition in ion-molecule collision. The contribution of collective excitation is distinctly identified in ionization and evaporation processes (H , $2H$, C_2H_2 loss) in proton (50-180 keV) collision experiments with gaseous naphthalene at IUAC, New Delhi using an electron cyclotron resonance ion source. The photoelectron spectroscopy with pyrene and fluorene showed that collective excitation is coupled to inner valence shell and hence a good amount of excitation energy goes in heating

which leads to above evaporation process. In the direct ionization mode, two mechanisms are active in the collision process: large impact parameter plasmon excitation mode and closer encounters with higher amount of electronic energy loss leading to fragmentation, whereas the resonant electron capture process was found to be associated with less electronic energy loss.

MO 13.5 Wed 12:15 PH/SR106

Collective excitation in energetic proton collision with naphthalene — ●PREETI M MISHRA^{1,2}, JYOTI RAJPUT³, C P SAFVAN⁴, SARITA VIG¹, and UMESH KADHANE¹ — ¹Indian Institute of Space Science and Technology, Trivandrum-695547, India — ²Max-Planck-Institut für Kernphysik, Saupfercheckweg 1, 69117 Heidelberg, Germany — ³University of Delhi, Delhi-110 007, India — ⁴Inter-University Accelerator Centre, Aruna Asaf Ali Marg, New Delhi-110 067, India

The structural and dynamical study for Polycyclic aromatic hydrocarbons (PAHs) is important in astrophysics as well as in medical science. Due to delocalized electrons, PAHs show collective excitation characterized by large oscillator strength which are difficult to isolate from other physical processes due to broader energy deposition in ion-molecule collision. The contribution of collective excitation is distinctly identified in ionization and evaporation processes (H , $2H$, C_2H_2 loss) in proton (50-180 keV) collision experiments with gaseous naphthalene at IUAC, New Delhi using an electron cyclotron resonance ion source. The photoelectron spectroscopy with pyrene and fluorene showed that collective excitation is coupled to inner valence shell and hence a good amount of excitation energy goes in heating which leads to above evaporation process. In the direct ionization mode, two mechanisms are active in the collision process: large impact parameter plasmon excitation mode and closer encounters with higher amount of electronic energy loss leading to fragmentation, whereas the resonant electron capture process was found to be associated with less electronic energy loss.

MO 13.6 Wed 12:30 PH/SR106

ICD in He droplets induced by electron-ion recombination — ●MARCEL MUDRICH¹, AARON LAForge¹, FRANK STIENKEMEIER¹, ROBERT MOSHAMMER², and THOMAS FENNEL³ — ¹Universität Freiburg — ²Universität Rostock — ³MPI für Kernphysik, Heidelberg

The photoionization dynamics of helium droplets irradiated by EUV light is studied using synchrotron radiation and photoelectron-photoion coincidence imaging spectroscopy. At photon energies > 46 eV, secondary processes such as elastic and inelastic electron-helium scattering become important. For large droplets ($> 10^6$ atoms), an additional ionization channel dominates even over direct ionization – interatomic Coulombic decay (ICD) induced by electron impact excitation and electron-ion recombination. We present a combined experimental and theoretical study of the dynamics of ionization of large He droplets at high photon energies.

MO 13.7 Wed 12:45 PH/SR106

Rotational Angular Momentum Polarisation of HCl and HF in $H+FCI(v=0-5, j=0-9) \rightarrow HCl+F$ and $HF+Cl$ at $E_{rel} = 0.5-20$ kcal/mol — ●VICTOR WEI-KEH CHAO — Department of Chemical and Materials Engineering, National Kaohsiung University of Applied Sciences, 80782 Kaohsiung, Taiwan, R.O.C. — Group 1101, State Key Laboratory of Molecular Reaction Dynamics, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023 P.R.C. — Victor Basic Research Laboratory e. V. D-33602 Bielefeld, Germany

QCT calculation with trajectories 100,000 for the title reactions on the DHTSN ground $1^2A'$ PES has been done. Having the early barrier patterns, both PESs with barrier heights 2.2 and 2.6 kcal/mol, at (2.05, 1.75) and (1.9, 1.7) Å, respectively, can cause bent intermediate $[HClF]$ and $[HFC]$ ca. 120° . Polar $p(\vartheta_r)$, azimuthal $p(\varphi_r)$, dihedral $p(\vartheta_r, \varphi_r)$ and PDDCS angular distr. of HCl and HF depend. upon $FCI(v, j)$ show, that both are at $\vartheta_r = 90^\circ$ for all E_{rel} , v and j ; at $\varphi_r = 270^\circ$ and 90° , respectively, for $FCI(v=0-2, j=0-9)$ at $E_{rel} \approx 5$ kcal/mol; both at $\varphi_r = 270^\circ$ for $FCI(v=2-5, j=0-9)$ at $E_{rel} \approx 15$ kcal/mol; for $FCI(v=0-5, j=0-9)$ at $E_{rel} \approx 0.5-1$ kcal/mol around E_{th} is uncertain; both are scattered back- ($\vartheta_t=180^\circ$) and forwards (90°); both are strongly aligned at $E_{rel} \leq 1$ kcal/mol. Influence of E_{rel} becomes decisive at $E_{rel} \geq 5$ kcal/mol, independ. on v or j . Intergration of a higher PES might unnecessary. Support with QCT-PDDCS code by K-L. Han, Group 1101, and financial aids by DICP, CAS (KF-2013-01, KF-2014-01), and VBR in Bielefeld are acknowledged. Ref. V.W.-K. Wu, *PCCP*. 13 (2011) 9407; 14 (2012) 16784; *Chin. Phys. B*, 22 (2013) 103101-1-13.

MO 14: Cold Molecules 2

Time: Wednesday 14:30–16:30

Location: PH/HS1

Group Report

MO 14.1 Wed 14:30 PH/HS1

Rotational cooling of trapped polyatomic molecules — ●ROSA GLÖCKNER, ALEXANDER PREHN, MARTIN IBRÜGGER, MARTIN ZEPPENFELD, and GERHARD REMPE — Max-Planck-Institut für Quantenoptik, Hans-Kopfermann-Str. 1, 85748 Garching, Germany

Due to their anisotropic long range interaction and many internal states, cold or ultracold polar molecular ensembles offer manifold possibilities for studying many-body physics and quantum information or quantum controlled collisions and chemistry. A prerequisite for all applications in quantum optics is thereby to gain and maintain control over the internal and external degrees of freedom.

In this talk, I present rotational state cooling of CH₃F molecules via optical pumping. We exploit vibrational transitions to optically pump 16 *M*-sublevels of four rotational states into a single *M* level. With the combination of rotational and motional cooling [1,2] we are thus able to produce a trapped and cold (30mK) ensemble of CH₃F molecules with more than 70% of all molecules populating the same single *M* state. We expect this method to be applicable to a wide variety of molecular species, thus opening a route for quantum controlled experiments with polyatomic molecules.

[1] M. Zeppenfeld *et al.*, *Phys. Rev. A* **80**, 041401 (2009).

[2] M. Zeppenfeld *et al.*, *Nature* **491**, 570-573 (2012).

MO 14.2 Wed 15:00 PH/HS1

Mikrosolvation of Phthalocyanine in superfluid Helium nanodroplets revisited — TOBIAS PREMKE, PHILIPP MEIER, and ●ALKWIN SLENCZKA — Universität Regensburg, 93053 Regensburg, Germany

Phthalocyanine was one of the first molecules investigated in superfluid Helium droplets by means of electronic spectroscopy [1, 2]. It became one of the best investigated organic dopant species. Inhomogeneous line broadening [3, 4], rotational fine structure [5], excited state life times [6], the Helium solvation layer [7-9], and the corresponding phonon wing [2, 10] have been studied by fluorescence excitation spectra and for some of the phenomena in combination with dispersed emission spectra. A recent resumption of electronic spectroscopy of Phthalocyanine in superfluid Helium droplets revealed new and unexpected results which put some of the previously reported results into question. Besides revisions of some particular details the recent study will be contrasted with the current understanding of microsolvation in superfluid Helium droplets.

[1] M. Hartmann, PhD Thesis, Göttingen, 1997. [2] M. Hartmann *et al.*, *Phys.Chem.Chem.Phys.*, **4** (2002) 4839. [3] A. Slenczka *et al.*, *J.Chem.Phys.* **115** (2001) 10199. [4] B. Dick, A. Slenczka, *J.Chem.Phys.* **115** (2001) 10206. [5] R. Lehnig *et al.*, *J.Chem.Phys.* **121** (2004) 9396. [6] D. Pentlechner *et al.*, *J.Phys.Chem.A*, **115** (2011) 7034. [7] R. Lehnig, A. Slenczka, *J.Chem.Phys.* **118** (2003) 8256. [8] R. Lehnig, A. Slenczka, *ChemPhysChem*, **5** (2004) 1014. [9] R. Lehnig, A. Slenczka, *J.Chem.Phys.* **120** (2004) 5064. [10] R. Lehnig *et al.*, *J.Phys.Chem.A*, **111** (2007) 7576.

MO 14.3 Wed 15:15 PH/HS1

Time resolved photoion/electron imaging spectroscopy of Rubidium atoms attached to Helium nanodroplets — ●JOHANNES VON VANGEROW, OLIVER JOHN, FRANK STIENKEMEIER, and MARCEL MUDRICH — Physikalisches Institut, Universität Freiburg, Hermann-Herderstr. 3, 79104 Freiburg, Germany

This presentation will focus on a metallic dopand, Rubidium, forming a bound surface state with a liquid Helium nanodroplet. In a femtosecond pump probe experiment, we trigger the desorption of the dopand via resonant excitation of the surface state, i.e. the 6P Σ and 6P Π states in the pseudodiatomic model approach.

By subsequent ionization of the dopand and time of flight mass detection up to $6.4 \cdot 10^4$ amu, we observe solvation dynamics of the Rb⁺ occuring for delay times ≤ 1 ps. Mass selected velocity map images of the desorbed Rb⁺ and RbHe⁺ photofragments show an increasing kinetic energy and anisotropy leveling out at $t \leq 10$ ps for all excitation wavelengths. Vice versa, photoelectron images show a decreasing energy asymptotically reaching the corresponding atomic transition.

The experimental results will be compared to a semiclassical model particularly focusing on the RbHe⁺ formation dynamics involving assoziative photoionization.

MO 14.4 Wed 15:30 PH/HS1

High Resolution Infrared Spektropy and Semi-Experimental Structures of Silicon-Carbon and Germanium-Carbon Clusters — ●VOLKER LUTTER¹, SVEN THORWIRTH², JÜRGEN GAUSS³, and THOMAS GIESEN¹ — ¹Institut für Physik, Universität Kassel, Heinrich-Plett-Straße 40, Kassel — ²I. Physikalisches Institut, Universität zu Köln, Zùlpicher Straße 77, Köln — ³Institut für Physikalische Chemie, Johannes Gutenberg-Universität Mainz, Duesbergweg 10-14, Mainz

Gas-phase spectra of molecules and clusters comprising carbon and refractory elements like silicon and germanium are not well studied despite the relevance of these systems in various fields of research such as material sciences, nanotechnology, astrochemistry and theoretical chemistry. Especially for mixed polyatomic germanium-carbon molecules no high-resolution spectroscopic studies have been reported to date.

In this contribution, we present the first high-resolution gas-phase measurements of jet-cooled linear Ge₂C₃ (Ge=C=C=C=Ge). The rovibrational spectrum of the antisymmetric C-C-stretching mode ν_3 has been observed at 5.2 μm and found to exhibit a complex pattern due to the presence of a sizable number of abundant isotopologs. Our study is complemented by high-level quantum-chemical calculations of Ge₂C₃ at the CCSD(T) level of theory. The data analysis allows for direct comparison of theoretical and experimental results of selected molecular parameters.

MO 14.5 Wed 15:45 PH/HS1

Zeeman deceleration of metastable helium and nitrogen atoms — ●KATRIN DULITZ, JUTTA TOSCANO, ATREJU TAUSCHINSKY, and TIMOTHY P. SOFTLEY — Department of Chemistry, University of Oxford, Chemistry Research Laboratory, 12 Mansfield Road, Oxford, OX1 3TA, UK

Zeeman deceleration is an experimental technique in which strong inhomogeneous magnetic fields inside an array of solenoid coils are used to manipulate the velocity of a supersonic beam of paramagnetic atoms or molecules [1,2].

We present experimental results that demonstrate, for the first time, the Zeeman deceleration of helium atoms in the metastable ²3S₁ state and nitrogen atoms in the metastable ²D_{5/2} state. Using an electron-impact source and a short, 12-stage Zeeman decelerator, we achieve an up to 40% decrease in the kinetic energy of the metastable helium beam [3]. In a proof-of-principle experiment with metastable nitrogen atoms, we achieve deceleration from 460 m/s to 410 m/s. We also show that the pulse duration for electron-impact excitation needs to be matched to the acceptance of the decelerator in order to obtain a good contrast between the decelerated and undecelerated parts of the beam.

[1] N. Vanhaecke *et al.*, *Phys. Rev. A* **75**, 031402 (2007). [2] E. Narevicius *et al.*, *Phys. Rev. A* **77**, 051401 (2008). [3] K. Dulitz, A. Tauschinsky, T. P. Softley, *submitted*.

MO 14.6 Wed 16:00 PH/HS1

Photo-ejection of biomolecular ions from helium droplets — ●JENNY PESTEL, DOO-SIK AHN, ANA ISABEL GONZALEZ FLOREZ, and GERT VON HELDEN — Fritz-Haber-Institut der MPG, Berlin, Germany

Superfluid helium droplets are an ideal environment to investigate ions at cryogenic temperatures. By (photo-)excitation the ion can get ejected from the helium droplet. This process is not completely understood yet. Our goal is to characterize the photo-ejection process and shed more light on the underlying mechanism.

We have developed an experimental setup [1] where biomolecular ions are brought to the gas-phase via electrospray ionization. Subsequently they are mass/charge selected in the quadrupole mass filter and accumulated in a linear ion trap. A pulsed beam of helium droplets picks up the ions as they traverse the trap. From here the doped droplets can be accelerated and measurements as a function of flight time allow us to determine the ejection efficiency on size distributed droplets [2].

With this approach we can study the ion ejection for different dopants on the pre-defined helium droplet sizes. This makes it possible to analyze and report recent results using both ultraviolet as well as infrared light for photo-excitation.

- [1] F. Bierau et al., *Phys. Rev. Letter.* 105, 133402 (2010)
 [2] F. Filsinger et al., *PCCP*, 1-8 (2012)

MO 14.7 Wed 16:15 PH/HS1

Low energy scattering of Stark-decelerated OH radicals with ortho- and para-H₂ molecules — ●H.C. SCHEWE¹, X. WANG¹, S. Y. T. VAN DE MEERAKKER², G. MEIJER^{1,2}, Q. MA³, J. KLOS³, P. J. DAGDIGIAN³, M. H. ALEXANDER³, A. V. D. AVOIRD², and N. VANHAECKE^{1,4} — ¹Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany. — ²Radboud University Nijmegen, Institute for Molecules and Materials, Heijendaalseweg 135, 6525 AJ Nijmegen, the Netherlands. — ³Department of Chemistry and Biochemistry and Institute for Physical Science and Technology, University of Maryland, College Park, MD 20742-2021, USA. — ⁴Laboratoire Aime Cotton, CNRS, Université Paris-Sud, 91405 Orsay,

France.

The crossed beam scattering is an important experimental method to investigate molecular interactions, which can lead to energy transfer or chemical reactions. The Stark deceleration technique yields control over both the internal and external degrees of freedom of polar molecules in a molecular beam. The combination of these techniques opens up deeper investigations of molecular scattering processes as a function of the collision energy with a very high energy resolution.

Results on inelastic scattering of ortho- or para-H₂ with Stark-decelerated OH(X ²Π_{3/2,J}) = 3/2, f) at collision energies between 60-150 1/cm are presented. The main difference in the scattering process of ortho- and para-H₂ is seen in the relative cross sections, originating from the different multipole interactions involved and are compared with theory.

MO 15: Clusters in Molecular Physics (with A & MS)

Time: Wednesday 14:30–16:30

Location: PH/SR106

Invited Talk MO 15.1 Wed 14:30 PH/SR106
Vibrational Spectroscopy of Cluster Complexes with Free Electron Lasers: Surface Science en Miniature — ●ANDRÉ FIELICKE — Institut für Optik und Atomare Physik, Technische Universität Berlin, Germany

Transition metal clusters are frequently used as model systems for low coordinated sites of extended surfaces and their study can provide valuable insights into the mechanisms of surface reactions. In many cases, however, there is still a lack of information on their structures and the relationship between structure and chemical behavior. Using vibrational spectroscopy of gas-phase clusters one can obtain information about the clusters' structure or the behavior of adsorbed species. The latter provides valuable insights into the binding geometry, the activation of bonds within the ligands or reactions occurring on the clusters' surface. Cluster size specific data can be obtained using infrared multiple photon dissociation spectroscopy. To cover the required spectral range from the far to the mid-IR our experiments make use of IR free electron lasers. The talk will discuss exemplary studies about reactions on platinum clusters [1] and the activation of molecular oxygen by small gold clusters [2].

- [1] D.J. Harding, A. Fielicke, *Chem. Eur. J.* 20 (2014) 3258
 [2] A.P. Woodham, A. Fielicke, *Struct. Bond.* 161 (2014) 243

MO 15.2 Wed 15:00 PH/SR106

Vibrational spectra and structures of C, B, and N-doped silicon clusters — ●NGUYEN XUAN TRUONG, BERTRAM JAEGER, PHILIP JÄGER, MARCO SAVOCA, ANDRE FIELICKE, and OTTO DOPFER — IOAP, TU-Berlin, Germany

Doping Si clusters changes their physical and chemical properties in a way that might be promising for the miniaturization trend towards nanoelectronics. Here, we investigated Si clusters doped with C, B and N with resonant infrared-ultraviolet two-color ionization (IR-UV2CI) and global optimization coupled with electronic structure methods. Doped Si clusters are irradiated with tunable IR light from a Free Electron Laser before being ionized with UV photons from an F₂ laser. Resonant absorption of IR photons leads to an enhanced ionization efficiency for the neutral clusters and provides the size-specific IR-UV2CI spectra. Structural assignment of the clusters is achieved by comparing the experimental IR-UV2CI spectrum with the calculated linear absorption spectra of the most stable isomers. Low-energy isomers are found with the help of genetic and basin-hopping algorithms. For Si_mC_n (with m + n = 6), we observed the systematic transition from chain like geometries for C₆ to 3D structures for Si₆. We showed for the first row doped Si₆X (with X = Be, B, C, N, O) clusters that different structures, vibrational and electronic properties can be achieved depending on the nature of the dopant atom. All dopant atoms in Si₆X have a negative net charge suggesting that Si atoms act as electron donors within the clusters. Finally, vibrational spectra and structural assignments for B and N-doped Si clusters are discussed in detail.

MO 15.3 Wed 15:15 PH/SR106

(N)IR spectroscopy on two- and three-centered isolated cationic cobalt-, nickel- and cobalt/nickel - ethanol clusters — ●MARKUS BECHERER¹, DANIEL BELLAIRE¹, WEI JIN², GEORGIOS LEFKIDIS², WOLFGANG HÜBNER², and MARKUS GERHARDS¹ —

¹TU Kaiserslautern, Fachbereich Chemie, Erwin-Schrödinger-Straße 52, 67663 Kaiserslautern — ²TU Kaiserslautern, Fachbereich Physik, Erwin-Schrödinger-Straße 47, 67663 Kaiserslautern

Clusters containing transition metals and aliphatic ligands provide model systems regarding e.g. catalytical properties, magnetism, reactivity and structure. Thus, the successive variation of size and composition of the metal clusters can give a fundamental insight on possible cooperative effects. The investigated two- and three-centered pure and combined cationic cobalt, nickel clusters are produced by applying laser ablation to a rotating metal rod and by attaching the ethanol ligand in a supersonic beam. The frequencies and frequency shifts of OH and CH stretching vibrations (between different clusters) are probed by means of IR-photofragmentation spectroscopy. A structural assignment is performed by comparing the experimental data with calculated frequencies obtained from DFT calculations. In case of the isolated cationic (cobalt)₃(ethanol)₁ and (cobalt)₃(ethanol)₁(water)₁ clusters both IR and electronic spectra (in the NIR region) are investigated through photodissociation spectroscopy. The experimentally observed spectra serve, among other aspects, as reference for theoretical calculations especially on the electronic transitions localized on the triangular Co trimer metal centre.

MO 15.4 Wed 15:30 PH/SR106

First experiments with cooled clusters at the Cryogenic Trap for Fast ion beams — ●CHRISTIAN MEYER¹, KLAUS BLAUM¹, CHRISTIAN BREITENFELD^{1,2}, SEBASTIAN GEORGE¹, JUERGEN GOECK¹, JONAS KARTHEIN¹, THOMAS KOLLING³, JENNIFER MOHRBACH³, GEREON NIEDNER-SCHATTEBURG³, LUTZ SCHWEIKHARD², and ANDREAS WOLF¹ — ¹Max-Planck-Institut für Kernphysik, Saupfercheckweg 1, 69117 Heidelberg, Germany — ²Institut für Physik, Ernst-Moritz-Arndt Universität, 17487 Greifswald, Germany — ³Fachbereich Chemie, TU Kaiserslautern, Germany

The Cryogenic Trap for Fast ion beams (CTF) is an electrostatic ion beam trap for the investigation of charged particles in the gas phase located at the "Max-Planck-Institut für Kernphysik" in Heidelberg. It is suited to study thermionic and laser-induced electron emission of anions with complex multi-body structure such as clusters and molecules. They can be stored up to several minutes due to the low restgas pressure of 10⁻¹³ mbar [1] in an ambient temperature down to 15 K. The experiments were so far hampered by the ion production in a sputter source leading to excited particles with high rovibrational states. In order to be able to investigate the ground state properties of such systems a new supersonic expansion source [2] has been implemented. A laser-induced plasma is expanded into vacuum by short pulses (50 μs) of a helium carrier gas and thereby rovibrationally cooled. First tests with metal cluster will be presented and discussed.

- [1] M. Lange et al., *Rev. Sci. Instr.*, 81,055105 (2010)
 [2] C. Berg et al., *J. Chem. Phys.* 102, 4870 (1995)

MO 15.5 Wed 15:45 PH/SR106

Optical spectra and structures of C, N, and O-doped silicon clusters — ●BERTRAM K.A. JAEGER, JANINA LEBENDIG, NGUYEN X. TRUONG, ANDRE FIELICKE, and OTTO DOPFER — IOAP, TU Berlin, Germany

Controlled changes in physical and chemical properties of doped Si clusters provide promising candidates of nanostructures for optoelectronics, sensors or medicine. We study Si clusters doped with C, N and O via their photodissociation spectra and compare them with theoretical quantum chemical calculations. Ionic clusters are produced in a laser vaporization source, then irradiated with tunable visible light from an OPO laser in the range from 410 to 580 nm and characterized by a reflectron time-of-flight mass spectrometer. Absorption of photons leads to dissociation of the clusters, which is detected in the mass spectrum. Calculated absorption spectra are compared to experimental data for assignment of geometries and electronic parameters of the observed clusters. The most stable and low-energy isomers are found with the help of genetic and basin-hopping algorithms. All results will be compared to existing studies about IR-UV two color ionization of neutral and doped Si clusters.

Pristine and tagged Au clusters show absorption bands in the visible range and are used as a test system to verify the experimental principle.

MO 15.6 Wed 16:00 PH/SR106

Angular distribution of electron and photon emission from isolated SiO₂ nanoparticles excited by femtosecond laser pulses — ●EGILL ANTONSSON, INA HALFPAP, CHRISTOPHER RASCHPICHLER, VALERIE MONDES, JÜRGEN PLENGE, BURKHARD LANGER, and ECKART RÜHL — Physical Chemistry, Freie Universität Berlin, Takustr. 3, 14195 Berlin

We excite isolated spherical SiO₂ nanoparticles (diameter: 90 nm, size distribution: 8%) with intense femtosecond laser pulses ($\lambda=800$ nm, $\tau=80$ fs, Intensity: $1\text{-}3\cdot 10^{13}$ W/cm²) and study the angular distribution of emitted electrons and UV photons ($h\nu>8$ eV). The nanoparticles are prepared in an aerodynamically focused beam which propagates into a high vacuum system where excitation and photoionization occurs. This ensures that fresh sample is available to each laser pulse and rules out effects due to particle-particle interactions, sample charging, and radiation damage. For electron emission, a distinct angular dependence with respect to the polarization vector of the laser pulses

is observed, which varies for different photoelectron energies. High-energy photoelectrons are found to be emitted preferentially parallel to the polarization vector of the exciting laser photons, which is discussed in terms of an elastic scattering of continuum electrons at or near the surface of the nanoparticles. For low-energy photoelectrons, on the other hand, the angular dependence is quenched due to multiple inelastic scattering events of the photoelectrons in the nanoparticles which smears out angular effects.

MO 15.7 Wed 16:15 PH/SR106

Vibrationally resolved UV fluorescence of diamondoids — ●TORBJÖRN RANDER¹, ROBERT RICHTER¹, TOBIAS ZIMMERMANN¹, ANDRE KNECHT¹, ANDREA MERLI¹, CHRISTOPH HEIDRICH¹, RAMON RAHNER¹, THOMAS MÖLLER¹, MERLE I. S. RÖHR², JENS PETERSEN², ROLAND MITRIĆ², JEREMY E. DAHL³, and ROBERT M. K. CARLSON³ — ¹Institut für Optik und Atomare Physik, Technische Universität Berlin, Berlin, Deutschland — ²Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Würzburg, Deutschland — ³Stanford Institute of Materials and Energy Sciences, Stanford University

Diamondoids are a class of perfectly size- and shape selectable carbon nanoparticles, with a wide range of interesting properties. Due to the size-selectivity afforded by the diamondoids, they are ideal model systems for studying the photo-physics of hydrocarbon molecules of different sizes. We present a study of the size- and shape dependent energy resolved UV fluorescence of diamondoids, ranging from adamantane to pentamantane, using narrow band laser light as excitation source.

We conclude that previous, relatively straightforward interpretations of the fluorescence spectra recorded using synchrotron light are incomplete, and that the additional fine-structure observed in the laser excited spectra can only be properly assigned by performing computations, in our case DFT and TD-DFT was deemed sufficient to accurately describe and understand the spectral envelopes of the different sized diamondoids. The approach employed is thought to generally be applicable also for other hydrocarbon molecules.

MO 16: Posters 3: Novelties in Molecular Physics

Time: Wednesday 17:00–19:00

Location: C/Foyer

MO 16.1 Wed 17:00 C/Foyer

X-ray spectra of hemin in different solvents: theoretical approach — ●MARIE PREUSSE, SERGEY I. BOKAREV, and OLIVER KÜHN — Institut für Physik, Universität Rostock, 18051 Rostock

Metalloporphyrins are essential constituents of a variety of enzyme active centers and are important due to their catalytic activity and biological functions. Hemin, being one example, is of particular interest as it is the chlorine salt of the heme group, which is known to play a major role in the oxygen storage and transport in living beings. X-ray spectroscopic methods are a powerful tool to probe the local electronic structure. They have been used in previous investigations to derive the spin state of hemin and hemoglobin in physiological solution by Aziz et al. [1]

Recently, resonant X-ray absorption (XAS) and inelastic scattering (RIXS) spectra of hemin in DMSO and in water have been reported [2]. Hemin is known to form dimers in water solutions, staying monomeric in other solvents [3]. In the present work we address the fingerprints of dimerization in water solution in XAS and RIXS using Restricted Active Space SCF and State Interaction computational methods (RASSCF/RASSI). Thereby we take into account strong correlation effects as well as spin-orbit coupling.

[1] Emad F. Aziz et al. Phys. Rev. Lett., 102:068103-1, 2009.

[2] Kaan Atak et al. J. Phys. Chem. B, 118(33):9938, 2014

[3] Katherine A. de Villiers et al. JBIC, 12(1):101, 2007

MO 16.2 Wed 17:00 C/Foyer

Investigation of the photophysical properties and metal-metal-interactions in mono-, bi- and trinuclear Au complexes — ●ANNEKEN GRÜN¹, FABIAN DIETRICH¹, SIMON WALG², MERVE CAYIR², JESSICA RAHN¹, WERNER THIEL², and MARKUS GERHARDS¹ — ¹TU Kaiserslautern, Fachbereich Chemie, Physikalische und Theoretische Chemie, Erwin-Schrödinger-Str. 52, 67663 Kaiserslautern, Germany — ²TU Kaiserslautern, Fachbereich Chemie, Anorganische

Chemie, Erwin-Schrödinger-Str. 54, 67663 Kaiserslautern, Germany

Au complexes such as bispyrimidinyipyridine-(NH(CH₂)₂)₂PPh₂)₂ [AuCl]₂-(H) are of great interest in synthesis due to their catalytic activity e.g. for hydroarylation and hydroamination. We investigate structurally similar mono-, bi- and trinuclear Au complexes in solution to understand their photophysical behavior which is probably induced by cooperative effects. The ground state and electronically excited states are analyzed by the application of UV/Vis- and fluorescence spectroscopy as well as the time correlated single photon counting (TCSPC) technique to determine the lifetime of the excited states. Measurements of the metal free ligands are compared to the spectra of the complexes as well as time dependent density functional theory (TD-DFT) calculations are performed to explain the photophysical properties and the effects of metal-metal interactions. The influence of interactions resulting from one or two gold atoms as well as the impact of an additional zinc center on the emission spectra is discussed.

MO 16.3 Wed 17:00 C/Foyer

Ultrafast photochemistry of a carbonyl-nitrosyl molybdenum complex — ●JOHANNES KNORR¹, SEBASTIAN SCHOTT², JARNO RIEFER², CHRISTOPH NAGEL³, ULRICH SCHATZSCHNEIDER³, and PATRICK NUERNBERGER¹ — ¹Physikalische Chemie II, Ruhr-Universität Bochum, 44780 Bochum — ²Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany — ³Institut für Anorganische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

Transition-metal complexes capable of releasing small molecular messengers upon photoactivation are promising sources of gasotransmitters such as carbon monoxide (CO) or nitric oxide (NO) in biological applications [1]. Recently, we investigated the photochemistry of a water-soluble manganese tricarbonyl complex using femtosecond spectroscopy combined with DFT-calculations, and found that several elec-

tronic transitions in the UV may cause CO loss, but always just one CO-ligand is released on an ultrafast timescale [2]. In this study, we extend this approach to $[\text{Mo}(\text{CO})_2(\text{NO})(\text{py}_3\text{tacn})]\text{PF}_6$ with $\text{py}_3\text{tacn} = \text{tris}(2\text{-pyridylmethyl})\text{-}1,4,7\text{-triazacyclononane}$, a molybdenum complex containing both carbonyl and nitrosyl ligands, and explore the photolytic dynamics upon excitation by employing UV-pump/VIS-probe and UV-pump/IR-probe ultrafast spectroscopy. In particular, we are interested in how the photodynamics in mixed carbonyl-nitrosyl compounds differ from systems with only carbonyl ligands.

[1] U. Schatzschneider, *Eur. J. Inorg. Chem.* 2010, 10, 1451-1467

[2] P. Rudolf et al., *J. Phys. Chem. Lett.* 2013, 4, 596-602

MO 16.4 Wed 17:00 C/Foyer

Ultrafast dynamics of mixed trihalides in solution — ●SEBASTIAN SCHOTT, LEA RESS, JULIA HEITMÜLLER, ANJA HASENKOPF, FLORIAN KANAL, PATRICK NUERNBERGER, and TOBIAS BRIXNER — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

The Trihalide I_3^- is not only a very successful model system for ultrafast time-resolved spectroscopy [1], but also plays an important role in dye-sensitized solar cells [2]. Recently, the efficiency of such cells could be increased by adding the mixed trihalide I_2Br^- to the electrolyte [3]. Another feature of asymmetric mixed trihalides, e.g. BrICl^- , is the existence of two distinguishable chemical bonds. Therefore, in contrast to the symmetric triiodide, a photodissociation reaction may result in different fragments, e.g. $\text{BrICl} + h\nu \rightarrow \text{Br} + \text{Cl}$ or $\text{Br} + \text{ICl}$. We use transient absorption spectroscopy with supercontinuum white-light probe pulses to investigate possible reaction paths of several mixed trihalides with the aim to elucidate which parameters may have an impact on the outcome of the photoinduced dynamics. Especially, pronounced wave packet oscillations, observed during the first 3 ps, are promising for the identification of the newly formed products.

[1] U. Banin, A. Waldman, S. Ruhman, *J. Chem. Phys.* 1992, 96, 2416

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

[3] N. C. D. Nath, H. J. Lee, W.-Y. Choi, J.-J. Lee, *Electrochim. Acta* 2013, 109, 39

MO 16.5 Wed 17:00 C/Foyer

Pump-Probe Photo-Ionization Experiments in a Collinear Phase Modulation Scheme — ●MARCEL BINZ, LUKAS BRUDER, DANIEL UHL, MARCEL MUDRICH, AARON LAFORGE, and FRANK STIENKEMEIER — Physikalisches Institut, Universität Freiburg, Germany

Due to the low target densities in molecular beam experiments, coherent fs spectroscopy of these systems has remained a challenging task. Within this context, we are investigating a phase-modulation technique established by Marcus *et al.* [1]. In this fs pump-probe scheme, the signal to noise ratio is greatly improved by combining continuous acousto-optical phase modulation with lock-in detection. One drawback of this method is its requirement of a high repetition rate laser system to sufficiently sample the modulation frequency.

Using a 80MHz Ti:Sa oscillator, we have so far applied this scheme to investigating alkali metals by means of fluorescence detection in a vapor cell as well as photo electron and mass resolved photo ion detection in a molecular and a doped helium droplet beam. The implementation of this method into a 5kHz repetition rate laser system is discussed in view of applications to even lower repetition rate lasers.

[1] P. F. Tekavec, T. R. Dyke, and A. H. Marcus, *J. Chem. Phys.* 125, 194303 (2006).

MO 16.6 Wed 17:00 C/Foyer

XUV Transient Absorption Spectroscopy of Photochemical Processes — ●LORENZ DRESCHER, MARTIN GALBRAITH, JUDITH DURA, CHRISTOPHER SMEENK, MARC VRAKING, and JOCHEN MIKOSCH — Max-Born-Institut, Berlin, Germany

The exact position of atomic inner-shell absorption edges depends sensitively on the atom's chemical environment. Chemical shifts hence allow to identify specific sites in a molecule with absorption spectroscopy. Ultrashort, spectrally broad XUV pulses from High Harmonic Generation offer the intriguing opportunity of transient absorption studies with unprecedented time resolution. It is anticipated that this will allow to access electronic and nuclear dynamics in molecules down to a few-femtosecond and even attosecond timescale from a site-specific point of view. Here we use this novel technique to study one of the reference standards of femtochemistry, the photodissociation of methyl iodide: $\text{CH}_3\text{I} + h\nu \rightarrow \text{CH}_3 + \text{I}$. The excitation of a single state in the A-band of CH_3I leads to a dissociation into CH_3 and both $\text{I}(^2\text{P}_{3/2})$ and

$\text{I}^*(^2\text{P}_{1/2})$ within 60-120 fs. This involves internal conversion at a non-adiabatic intersection within the first 20 fs after the Frank-Condon region [1]. Such fast time scales are a challenge for traditional femtochemistry experiments. We are also working on creating isolated attosecond pulses, which would pave the way to studying purely electronic dynamics in molecules with transient absorption. [1] Hammeric et al., *J. Chem. Phys.* 101, 5623 (1994), Corrales et al., *Nature Chemistry* 6, 785-790 (2014)

MO 16.7 Wed 17:00 C/Foyer

Towards multi-dimensional Raman spectroscopy of excited electronic states in the time domain — ●TORSTEN WENDE, CHRISTOPH SCHNEIDERMAN, MATZ LIEBEL, and PHILIPP KUKURA — Physical & Theoretical Chemistry Laboratory, South Parks Road, Oxford OX1 3QZ

Many biological and chemical processes rely on an efficient transfer of photon energy into specific atomic motion. Following the nuclear motion directly after photoexcitation provides valuable structural information to elucidate the mechanism that governs the energy flow throughout a molecule. We have developed a time-domain approach for measuring time-resolved excited-state Raman spectra by means of population-controlled impulsive vibrational spectroscopy. Using an ultrashort actinic (<15 fs) and impulsive (<10 fs) pump pulse in combination with a narrowband dump control pulse allows us to experimentally isolate excited-state vibrational coherence and follow its temporal evolution. Here, we study the fast internal conversion (<100 fs) from the S2 into the S1 electronic state in diphenyl-octatetraene. The time-resolved Raman spectra reveal that vibrational coherence is efficiently transferred from S2 into S1. We observe large amplitudes in the 850, 1300 and 1550 cm^{-1} modes which decay according to the S2 lifetime, while the remaining modes decay primarily with the lifetime of S1. Extraction of a 2D correlation map exhibits signatures of vibrational coupling indicated by multiple cross-peaks between low-frequency modes and selected high-frequency modes.

MO 16.8 Wed 17:00 C/Foyer

Imaging ultrafast molecular dynamics by strong-field ionization — ●FLORIAN BACH, FELIX BRAUSSE, FARUK KRECINIC, ARNAUD ROUZEE, and MARC VRAKING — Max-Born-Institut, Berlin, Germany

We investigated the vibrational wave packet dynamics in I_2 molecules following excitation by a 550 nm, 50 fs, pump laser pulse. The molecular motion was mapped into the photoelectron and photoion momentum distributions resulting from strong-field ionization by a 1300 nm probe laser pulse. Both momentum distributions were recorded with a velocity map imaging spectrometer (VMIS). The kinetic energy distribution of the I^+ fragments shows a clear signature of the vibrational wave packet motion induced by the pump laser pulse. We observe as well a modification of the angular distribution of the high kinetic energy photoelectrons that result from laser induced electron rescattering with the time delay between the two pulses that we assign to the change of the internuclear distance of the molecule.

MO 16.9 Wed 17:00 C/Foyer

Ultrafast Exciton Dynamics at a P3HT-Gold Interface Investigated by Femtosecond Time-resolved Pump-Probe Scanning Near-Field Microscopy — ●TAHIR ZEB KHAN, PATRICE DONFACK, MEHDI MOHAMMAD KAZEMI, SIDHANT BOM, VEIT WAGNER, and ARNULF MATERNY — Jacobs University, Campus Ring 1, 28759 Bremen, Germany

We demonstrate that femtosecond transient absorption spectroscopy in combination with scanning near-field optical microscopy (SNOM) is a powerful technique for obtaining a realistic picture of local exciton dynamical processes in organic semiconductor devices. Here, we present the study of exciton dynamics at the interface between a regioregular P3HT layer and a gold contact. Early exciton dynamics are determined by the available ultrafast decay pathways of hot excitons, which can form e.g. interfacial charge transfer excitons. This affects the overall exciton relaxation locally. Highly localized details are however not accessible via diffraction-limited spectroscopic techniques. We show that only when high spatial resolution is achieved, the local ultrafast exciton dynamics in P3HT (1-2 ps) is experimentally observed and proven to be significantly faster at the Au-P3HT interface as compared to neat P3HT. Moreover, we have observed that within 15 ps the overall relaxation from the probed excited state is at least 17 % less at the interface, which clearly indicates the formation of additional long-lived trapped states. The present results provide the first

experimental observation and evidence that the fate of hot excitons significantly determines the photophysics at the Au-P3HT interface.

MO 16.10 Wed 17:00 C/Foyer

Investigation of the chirality of halothane — ●PHILLIP BURZYNSKI¹, GREGOR KASTIRKE¹, MARTIN PITZER¹, MARKUS WAITZ¹, JONATHAN NEFF¹, MIRIAM WELLER¹, DANIEL METZ¹, ROBERT BERGER², REINHARD DÖRNER¹, and MARKUS SCHÖFFLER¹ — ¹Institut für Kernphysik, Goethe Universität, Frankfurt am Main — ²Fachbereich Chemie, Philipps-Universität, Marburg

The investigation of the chirality of complex carbon-based molecules is one important task in various research fields, e.g. biology, pharmacy, chemistry. Physics is looking for examples, where parity is not maintained. State of the art methods allow only to identify the absolute configuration of crystal structured samples by x-rays.

We investigated the chirality of halothane (C₂HBrClF₃) by using synchrotron radiation of various polarization. Halothane is an inhalative general anesthetic and consists of one more carbon-atom than formerly used targets. Analyzing the fragments in a ColTRIMS set up (Cold Target Recoil Ion Momentum Spectroscopy) can reveal information about the molecular structure. We are able to look at the different reaction channels (up to five ions) and identify the chirality of every ionized target-molecule.

MO 16.11 Wed 17:00 C/Foyer

Computing and comparing different molecular paths which could lead to the formation of CCH⁻ in the ISM — ●IBROKHIM ISKANDAROV¹, FABIO CARELLI¹, FRANCO A. GIANTURCO^{1,2}, and ROLAND WESTER¹ — ¹Institute for Ion Physics and Applied Physics, University of Innsbruck, 6020 Innsbruck, Austria — ²Scuola Normale Superiore, Pisa, 56125, Italy

Among the most important addressed questions currently involving molecular anions in the Interstellar Medium (ISM), one which has been not yet fully answered relates how this species are produced in different astrophysical regions where specific environmental conditions are expected to be at play. Recent astrochemical models support the formation of large anionic carbon chains C_nH⁻ (n=4,6,8) [1] while between the smallest molecular anions observed, the CCH⁻ has been only tentatively detected. We have thus undertaken an accurate theoretical and computational investigation on two specific interconnected mechanisms by which CCH⁻ (X¹Σ_g⁺) can be formed. Our computed rate coefficients for all the above, interconnected processes at the related environmental, local temperatures, shall be presented and discussed.

[1] F. Carelli, T. Grassi, M. Satta, F.A. Gianturco, ApJ **774**, 97 (2013)

MO 16.12 Wed 17:00 C/Foyer

Towards electron-impact ionization dynamics of biologically relevant molecules in a reaction microscope — ●THOMAS PFLÜGER¹, XUEGUANG REN², MARVIN WEYLAND¹, WOONYONG BAEK¹, ALEXANDER DORN², and HANS RABUS¹ — ¹Physikalisch-Technische Bundesanstalt, Bundesallee 100, 38116 Braunschweig — ²Max-Planck-Institut für Kernphysik, Saupfercheckweg 1, 69117 Heidelberg

After decades of investigation of the ionization dynamics of simple atoms and molecules in electron collision experiments, in recent years significant progress was being made in the study of more complex and finally biologically relevant targets (e.g. [1-3]). Our aim is to provide high-differential ionization cross sections and insight into fragmentation dynamics. Experimentally this is accessible by using an advanced reaction microscope (REMI) which was modified for electron impact experiments. Hence, it is possible to extract electronic information in form of e.g. triple-differential cross sections as well as fragmentation informations like kinetic energy release and molecular orientations. First results are presented for simple molecules as test candidates (e.g. CH₄) and tetrahydrofuran.

A detailed overview of the project and the employed methods and their performance will be presented.

[1] M. Dampc *et al.* 2011 *J. Phys. B* **44** 055206 [2] S. M. Bellm *et al.* 2012 *J. Chem. Phys.* **136** 244301 [3] W. Y. Baek *et al.* 2012 *Phys. Rev. A* **86** 032702

MO 16.13 Wed 17:00 C/Foyer

Electronic structure of thionized diamondoids. — ●THERESA HÖHNE¹, ANDRÉ KNECHT¹, ROBERT RICHTER¹, TOBIAS ZIMMERMANN¹, ANDREA MERLI¹, PAUL KAHL², PETER SCHREINER²,

THOMAS MÖLLER¹, and TORBJÖRN RANDE¹ — ¹Institut für Optik und Atomare Physik, Technische Universität Berlin — ²Institut für Organische Chemie, Justus-Liebig-Universität Giessen

Diamondoids, a fascinating class of mass and shape selected, hydrogen passivated, sp³-hybridized carbon nano-cages, allow a direct tuning of their properties through functionalization. Since pristine diamondoids show intrinsic UV photoluminescence, sulfurization is a promising step to alter their optical gap to the VIS/IR spectral region by varying the number of thione groups [1].

We investigated the electronic structure of this new group of functionalized nanodiamond, diamondoid thiones. For our purpose adamantane-2-thione up to higher cage structures such as [1(2,3)4]pentamantane-6-thione were studied. To measure spectra of the sublimated diamondoids we used synchrotron radiation at BESSY II and an OPO laser system to cover a broad spectral region. In addition we performed DFT calculations which assist in the interpretation of our experimental findings. We present the first results from valence photoelectron-, absorption- and fluorescence spectroscopy.

[1] M. Vörös, T. Demjén, T. Szilvási, und A. Gali, Phys. Rev. Lett. **108**, 267401 (2012).

MO 16.14 Wed 17:00 C/Foyer

Diagnostics of translational energy distribution of ions in 22 pole trap. — ●OLGA LAKHMANSKAYA, THORSTEN BEST, SUNIL KUMAR, ERIC ENDRES, DANIEL HAUSER, and ROLAND WESTER — Institute for Ion Physics and Applied Physics, University of Innsbruck, 6020 Innsbruck, Austria

Today the study of ion-molecule reactions moves towards cold chemistry which implies well-controlled ion ensembles and environment. The storage and preparation of ions by buffer gas cooling in multiple rf ion traps (such as: 16 or 22 pole) is a well established and robust technique. Nevertheless, a number of authors reveal the discrepancy between ion translational temperature and buffer gas temperature and the assignment of the temperature to the ion ensemble stay challenging. Here we present an experimental technique for diagnostics of highly energetic ions (OH⁻ and D⁻) in the trap (22 pole trap in our case). This scheme is based on the strong dependence of the lifetime of the ions on buffer gas temperature. It reveals a cutoff temperature of 20-25 K when the losses of ions terminates and therefore ion energy distribution should stay constant. Simulations of the ion distribution in the 22 pole trap help to shed light on the translational energy distribution of ions in the trap. [1] O. Y. Lakhmanskaya *et al.*, Int. J. Mass. Spectrom., 365, 281, 2014

MO 16.15 Wed 17:00 C/Foyer

Implementation of a pulsed nozzle in a cold reactive scattering setup — ●HANNA-SOPHIE MAIER, JONAS GRZESIAK, FRANK STIENKEMEIER, and MARCEL MUDRICH — Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str.3, 79104 Freiburg

The investigation of cold reactive scattering processes requires a dense and cold beam of metastable atoms and molecules. To this end a pulsed, supersonic and cryogenic nozzle including a home built dielectric barrier discharge (DBD) is used. We combine the beam of metastables with a second velocity-tunable molecular beam generated by a rapidly rotating nozzle. We present the characterization of the cold and dense beam of metastable atoms from the optimized pulsed nozzle setup. Moreover first results on reactive scattering of the metastables in the merged beam geometry are shown.

MO 16.16 Wed 17:00 C/Foyer

A new setup for merged-beam ion-neutral collision studies — PITT ALLMENDINGER, ●JOHANNES DEIGLMAYR, JOSEPH AGNER, HANSJÜRGEN SCHMUTZ, and FRÉDÉRIC MERKT — Laboratory of Physical Chemistry, ETH Zürich, Switzerland

Collisions between atoms or molecules in Rydberg-Stark states and atoms or molecules in the ground state can yield important information about the corresponding ion-neutral reaction: the Rydberg electron in the Rydberg-Stark states is almost entirely decoupled from the ion core and orbits around it at distances much larger than those at which typical ion-molecule reactions take place. Consequently, it does not influence the outcome of an ion-molecule reaction [1].

Recently we have demonstrated the simultaneous deceleration and deflection of H₂ molecules in Rydberg states following supersonic expansion from a reservoir at liquid-nitrogen temperature [2], yielding cold (T=100 mK) samples of H₂^{*} molecules with tunable velocities.

The combined decelerator and deflector is realized by a 50mm long two-dimensional array of electrodes on a printed circuit board which is bend to a deflection angle of 10° . We have integrated the device into a merged-beam setup, and observe the formation of H_3^+ ions from the collisions between H_2 ground-state and H_2 Rydberg molecules.

[1] S. T. Pratt, J. L. Dehmer, P. M. Dehmer, and W. A. Chupka, *J. Chem. Phys.* **101**, 882 (1994); [2] P. Allmendinger, J. Deiglmayr, J. A. Agner, H. Schmutz, and F. Merkt, *Phys. Rev. A* **90**, 043403 (2014)

MO 16.17 Wed 17:00 C/Foyer

Rotational state detection of trapped polyatomic molecules — ●ALEXANDER PREHN, ROSA GLÖCKNER, MARTIN IBRÜGGER, MARTIN ZEPPENFELD, and GERHARD REMPE — Max-Planck-Institut für Quantenoptik, Hans-Kopfermann-Str. 1, 85748 Garching

Many applications of cold and ultracold molecules benefit from the ability to detect internal states. Well established detection schemes (e.g. REMPI, LIF) often rely on excitations of electronic states which can lead to rapid predissociation, especially for many polyatomic molecular species, limiting their use.

Here, we present an alternative method based on depletion of molecules in selected rotational states from our electric trap [1]. The narrow electric field distribution inside the trap [2] allows us to spectroscopically address the desired states and couple them to untrapped states, thus removing their population from the trap. The difference of signals with and without depletion then constitutes the state selective molecule signal. We investigate two schemes exploiting rotational and/or vibrational transitions to detect sets of rotational states. Experimental data obtained with methyl fluoride (CH_3F) agrees nicely with rate equation models examining the dynamics of the process [2]. Additionally, we show signals originating from population in a single M -sublevel of a rotational state $|J, K, M\rangle$. We expect our method to work for a large number of molecular species.

[1] B.G.U. Englert *et al.*, *Phys. Rev. Lett.* **107**, 263003 (2011).

[2] R. Glöckner *et al.*, *arXiv:1411.7860* (2014).

MO 16.18 Wed 17:00 C/Foyer

IR spectroscopy of the ν_2 band of the water monomer solvated in helium droplets — ●RAFFAEL SCHWAN, THEO FISCHER, GERHARD SCHWAAB, and MARTINA HAVENITH — Ruhr-University Bochum, 44801 Bochum, Germany

High-resolution infrared spectra have been obtained in the frequency range of the ν_2 band of water solvated in superfluid helium droplets. Helium droplets provide an ultracold matrix at a temperature of 0.37 K. At this temperature only vibrational and rotational ground states of solvated molecules are populated. The spectra of water in helium droplets contain transitions from the rotational states 0_{00} and 1_{01} of the vibrational ground state since these states belong to different nuclear spin symmetry species. Due to slow nuclear spin relaxation in helium droplets a population ratio of about 1:3 is expected. For the water monomer a total of three bands has been found for the HOH ν_2 bending mode between 1600 and 1700 cm^{-1} . The bands were assigned to the three energetically lowest ro-vibrational transitions $\nu_2[1_{10} \leftarrow 1_{01}]$, $\nu_2[1_{11} \leftarrow 0_{00}]$ and $\nu_2[2_{12} \leftarrow 1_{01}]$. Rotational constants and rotational relaxation times can be estimated for the ro-vibrational transitions of the ν_2 bending mode analogous to previous results for the ν_1 and ν_3 stretching modes in helium droplets [1,2].

[1] K.E. Kuyanov, M.N. Slipchenko, A.F. Vilesov, *Chem. Phys. Lett.* **427** (2006) 5-9.

[2] C.M. Lindsay, G.E. Douberly, R.E. Miller, *J. Mol. Struct.* **786** (2006) 96-104.

MO 16.19 Wed 17:00 C/Foyer

Large amplitude vibrational motion of fullerenes — ●JAN HANDT and RÜDIGER SCHMIDT — Institut für Theoretische Physik, Technische Universität Dresden, D-01062 Dresden, Germany

In the optical laser regime two-colour pump-probe experiments in combination with nonadiabatic molecular dynamics calculations have revealed the excitation of a giant breathing motion in C_{60} [1]. Further theoretical studies showed the strong orientation dependence of energy absorption and subsequent relaxation dynamics leading to large amplitude vibrational motion up to symmetric fission processes [2]. Here, we extend these calculations and investigate large collective nuclear excitations in fullerenes up to the XUV laser regime which is now feasible by FEL sources, using nonadiabatic quantum molecular dynamics methods (NA-QMD(-H)) [3].

[1] T. Laarmann *et al.*, *Phys. Rev. Lett.* **98**, 058302 (2007)

[2] M. Fischer, J. H., *et al.*, *Phys. Rev. A* **88**, 061403(R) (2013)

[3] M. Fischer, J. H. and R. S., *Phys. Rev. A* **90**, 012525 (2014)

MO 16.20 Wed 17:00 C/Foyer

Intensive Femtosekunden XUV Pulse für zeitaufgelöste Molekülspektroskopie aus höherer Harmonischen-Erzeugung eines Laserpulses — ●MARKUS PFAU, ULRIKE FRÜHLING, THOMAS GEBERT, FAWAD KARIMI und MARTIN RANKE — Institut für Experimentalphysik, Luruper Chaussee 149, 22761 Hamburg, Deutschland

Die Erzeugung von hohen Harmonischen eines Lasers in einem Edelgas ist eine Möglichkeit zur Erzeugung von kohärenter, intensiver und hochenergetischer Strahlung. Sie deckt dabei das Spektrum vom ultravioletten bis hin zum schwachen Röntgenbereich ab und bietet die Möglichkeit, ultrakurze Pulse im Femto- bis Attosekunden Bereich zu erzeugen. Diese Pulse werden beispielsweise genutzt, um zeitaufgelöste Spektroskopie zu betreiben.

Es werden verschiedene Methoden zur Erzeugung hoher Harmonischer vorgestellt und entsprechend der experimentellen Randbedingungen zwei Konzepte ausgewählt und deren Aufbau dargestellt. Im ersten Aufbau wird dabei ein Zwei-Farben-Konzept mit schwachem Fokus in eine gepulste Gasdüse genutzt, um hoch intensive Harmonische mit Photonenenergien im Bereich von 50 eV zu erzeugen. Im zweiten Aufbau hingegen wird ein einfarbiges Konzept mit stärkerer Fokussierung in eine längenvariable Gaszelle verfolgt, um Photonenenergien im Bereich von 90 eV zu erreichen. Die XUV Pulse werden mit intensiven THz-Strahlen überlagert und mittels Streaking für zeitaufgelöste Molekülspektroskopie genutzt.

MO 16.21 Wed 17:00 C/Foyer

Versatile concepts in cryo-spectroscopy of isolated metal clusters and complexes — ●JONATHAN MEYER, THOMAS KOLLING, and GEREON NIEDNER-SCHATTEBURG — Technische Universität Kaiserslautern, Germany

We aim to combine cryogenically cooled ion traps with laser spectroscopy as a powerful tool to probe the structure and dynamics of metal cluster ions and their interaction with adsorbed molecules. The clusters are generated either in a laser vaporization source or an electrospray ion source, guided by a hexapole, mass selected by a quadrupole and stored in a hexapole ion trap. By using pulses of cold buffer gas (ca. 4K), the investigated species can be cooled down to their vibrational ground state. Action spectroscopy based on tagging the investigated species with rare gas atoms or other weakly bound messenger molecules enables spectroscopy of otherwise inaccessible vibrational and rotational modes. In case of resonant absorption the messenger atom or molecule can then be detached, which leads to a detectable change in the resulting mass spectrum taken by a reflectron time of flight mass spectrometer. The value of this type of scheme has been shown by Jasik *et al.* [1] and our own group [2]. Two different spectroscopic schemes for high resolution one color IR spectroscopy and for a non resonant simulated raman process are discussed.

[1] J. Jasik *et al.*, *International Journal of Mass Spectrometry* **354-355** (2013) 204-210

[2] Dillinger, S., Mohrbach, J., Hewer, J., Gaffga, M., Niedner-Schatteburg, G., manuscript in preparation, 2015

MO 16.22 Wed 17:00 C/Foyer

Two color enhanced IRMPD spectroscopy of a homobinuclear silver complex — ●JOACHIM HEWER and GEREON NIEDNER-SCHATTEBURG — Fachbereich Chemie und Forschungszentrum OPTIMAS, Technische Universität Kaiserslautern, Germany

Mass spectrometry and IR spectroscopy in combination enable us to investigate isolated ionic species without interference from solvents, lattices or adsorbates. Utilizing a two laser setup, resonant two color IRMPD (infrared multi photon dissociation) is capable of enhancing fragmentation efficiencies, thus revealing vibrational bands, which may be hardly observable by single color IRMPD.^{[1][2]} We report studies on a dinuclear transition metal complex $[(Ag)_2(HCCA)(DDA)]^+$ ($HCCA = \alpha$ -cyano-4-hydroxycinnamic acid, $DDA = 1,3$ -dideaza-adenine). Structure identification arises from comparison of one- and two-color IRMPD spectra to calculated spectra from density functional theory (DFT). Our investigations elucidate the internal vibrational redistribution (IVR) process as a function of the frequency, intensity and time delay of the applied nanosecond IR pulses. In particular we focused on fragmentation yields as a function of laser intensity.

[1] Y. Nosenko, F. Menges and C. Riehn, G. Niedner-Schatteburg, *Phys. Chem. Chem. Phys.*, **2013**, *15*, 8171-8178.

[2] J. Lang, M. Gaffga, F. Menges, G. Niedner-Schatteburg, Phys. Chem. Chem. Phys., 2014, 16, 17417.

MO 16.23 Wed 17:00 C/Foyer

Investigation of direct and indirect coupling of an adsorbate to the surface in SERS — ●FAEZEH MOHAGHEGH, ALIREZA MAZAHERI TEHRANI, and ARNULF MATERNY — Jacobs University, Campus Ring 1, 28759 Bremen, Germany

The surface enhancement of Raman Spectroscopy for molecules adsorbed to coin metal surfaces is still not completely understood. Surface-enhanced Raman scattering (SERS) was up to now mainly applied and studied using roughened metal films or metal nanoparticles as substrates. Unfortunately, these systems suffer from poor reproducibility. As an alternative, one could use flat metallic surfaces

to achieve the better reproducibility, which is needed for fundamental research. However, due to phase matching conditions, the coupling of light to the surface plasmons in the metal is not straight forward. The most common setup to achieve this goal is called Kretschmann configuration. There, surface plasmon polaritons (SPPs) can be excited in a thin layer of a metal covering a prism surface when a specific angle of incidence is chosen for the internal reflection of a light beam, under which the phase matching condition is fulfilled. The enhanced evanescent field and the coupling of the electronic systems of metal and molecules then result in an increase of Raman scattering from molecules adsorbed to the metal surface. In our work, we present experimental results from Raman investigations using the Kretschmann arrangement. Specifically, we have investigated the direct and indirect coupling of adsorbate to the surface. In our fundamental study, dyes like Nile Blue are preferred, which are known for high SERS efficiency.

MO 17: Cold Molecules 3

Time: Thursday 11:00–13:00

Location: PH/HS1

Invited Talk

MO 17.1 Thu 11:00 PH/HS1

State-selective attachment of helium atoms to stored, cold molecular ions — ●SANDRA BRÜNKEN, LARS KLUGE, ALEXANDER STOFFELS, OSKAR ASVANY, and STEPHAN SCHLEMMER — I. Physikalisches Institut, Universität zu Köln, Germany

Helium atoms attach to molecular cations via inversely temperature-dependent ternary association processes, forming weakly bound (< 3 kcal/mol) He-M⁺ complexes. We investigate the kinetics of this process by storing a few thousand mass-selected ions in a temperature-variable cryogenic rf 22-pole ion trap in the presence of a high number density of He and following the temporal evolution of He_n-M⁺ complexes ($n < 6$). In this way the rate coefficients for ternary association and collision induced dissociation are obtained for a number of ions, e.g. H₃⁺, CH₅⁺, CD⁺, CF⁺, CO⁺, HCO⁺. The dependence of the ternary association rate coefficient on the vibrational and rotational excitation of the ions is observed. A detailed account of the underlying kinetics will be presented on the example of rotational excitation of CD⁺. This state-dependent complex formation rate is employed for sensitive action spectroscopy of the parent and complex ions [1,2]. Its apparent general applicability will be demonstrated with recent examples of high-resolution IR spectroscopy (LIICG - Laser Induced Inhibition of Complex Growth), and of purely rotational spectroscopy. In addition first results of IR pre-dissociation spectroscopy of stored He-M⁺ complexes will be presented.

[1] Asvany et al., Applied Physics B **114**, 203 (2014); [2] Brünken et al., ApJL **783**, L4 (2014)

MO 17.2 Thu 11:30 PH/HS1

Cooperative effects of the hyperfine and Zeeman structure in the A – b state of Rb₂ — ●MARKUS DEISS¹, BJÖRN DREWS¹, EBERHARD TIEMANN², and JOHANNES HECKER DENSCHLAG¹ — ¹Institut für Quantenmaterie, Universität Ulm, 89069 Ulm, Germany — ²Institut für Quantenoptik, Leibniz Universität Hannover, 30167 Hannover, Germany

We have studied the hyperfine and Zeeman structure of spin-orbit coupled A¹Σ_u⁺ – b³Π_u states of Rb₂ molecules with small angular momentum ($J = 1$). For this purpose, Feshbach molecules trapped in a 3D optical lattice are irradiated by cw-light of a diode laser. In a frequency scan, resonant excitation of an energy level of the A – b manifold causes molecular losses. We observe surprisingly large total hyperfine/Zee-man splittings of up to 150 MHz at a magnetic field of 1000 G. Furthermore, we find that the hyperfine/Zee-man structures of various vibrational states differ substantially. We explain the data as follows: The measured level structures arise in second order from hyperfine and Zeeman interactions which cooperatively mix the 0_v⁺ and 0_v⁻ components of the b³Π_u state that are separated due to spin-orbit coupling. We can use our measurements to estimate the energy splitting between 0_v⁺ and 0_v⁻ for various vibrational levels.

MO 17.3 Thu 11:45 PH/HS1

Optimized Stark deflection and mixed-field orientation of OCS molecules — ●JENS S. KIENITZ^{1,2}, SEBASTIAN TRIPPEL¹, KAROL DLUGOLECKI¹, ROSARIO GONZÁLEZ-FÉREZ^{2,3}, and JOCHEN KÜPPER^{1,2,4} — ¹Center for Free-Electron Laser Science, DESY — ²Center for Ultrafast Imaging, University of Hamburg — ³Instituto

Carlos I, Universidad de Granada — ⁴Department of Physics, University of Hamburg

We demonstrate the use of very strong static electric fields to improve the well-known techniques to state-select molecules in the electric deflector and to mixed-field orient them using laser pulses in combination with strong electric fields. These are important methods for molecular-frame imaging of molecular dynamics [1, 2]. For the state selection we developed a Stark deflector with a so-called b-type shape. Simulations of the new design predict a much stronger deflection and better state separation than previous Stark deflectors. In mixed-field orientation a strong static electrical field avoids nonadiabatic effects [3]. Therefore, we extended the idea of a two plate velocity map imaging spectrometer [4] to allow for strong electric fields up to 27 kV/cm. We will present its use in alignment and orientation experiments and disentangle the rotational motion of molecules in combined strong electric fields and laser pulses.

[1] Holmegaard et al., *Nat. Phys.* **6**, 428 (2010)

[2] Küpper et al., *Phys. Rev. Lett.* **112**, 083002 (2014)

[3] Nielsen et al., *Phys. Rev. Lett.* **108**, 193001 (2012)

[4] Papadakis and Kitsopoulos, *Rev. Sci. Instr.* **77**, 083101 (2006)

MO 17.4 Thu 12:00 PH/HS1

Toward Controlling Large Molecules — ●NICOLE TESCHMIT¹, DANIEL HORKE¹, and JOCHEN KÜPPER^{1,2} — ¹Center for Free-Electron Laser Science, DESY — ²Department of Physics and Center for Ultrafast Imaging, University of Hamburg

The control of small gas-phase molecules has been experimentally demonstrated. This includes the separation of different conformers [1], the alignment and orientation of molecules in space [2], and the separation of different quantum states or clusters by using static and/or dynamic electric fields [3].

We are now working toward applying these techniques to larger molecules. This requires internally cold gas-phase molecules with high density, which will be produced with a new laser-desorption setup. By controlling large molecules structural and dynamic information can be gained from X-ray or electron diffractive imaging experiments, for example at free-electron lasers [4].

[1] Y.P. Chang et al, *Science* **342**, 98

[2] L. Holmegaard et al, *Nat. Phys.* **6**, 428

[3] D. A. Horke et al, *Angew. Chem. Int. Ed.* **53**, 1

[4] J. Küpper et al, *Phys. Rev. Lett.* **112**, 083002

MO 17.5 Thu 12:15 PH/HS1

Observation of molecular dimers in IR absorption Spectra of liquid hydrogen isotopologues — ●ROBIN GROESSLE and SEBASTIAN MIRZ — Karlsruhe Institute of Technology (KIT), Institute of Technical Physics (ITEP), Tritium Laboratory Karlsruhe (TLK)

One of the main tasks of the Tritium Laboratory Karlsruhe (TLK) is the development of analytical methods for hydrogen isotopologues. A promising method for liquid hydrogen is IR absorption spectroscopy. For this a cryogenic sample cell, able to liquefy the hydrogen isotopologues, with an open beam path for IR light, has been developed and set up.

This talk will focus on the contribution of hydrogen dimers in the

liquid phase to the IR spectra. The dimer model predicts non linear effects in the IR spectra. Thus the comparison of several spectra from different samples, including hydrogen, deuterium and mixtures enables a clear identification of dimers. In the case of pure H₂ a bunch of lines in between 8000 cm⁻¹ to 8800 cm⁻¹ and for D₂ between 5900 cm⁻¹ to 6500 cm⁻¹, both corresponding to the 2nd vibrational branch of homomolecular dimers, are observed. A third spectrum of mixed H₂ and D₂ then shows in addition several lines in between, corresponding to heteromolecular dimers. In addition these measurements have been repeated with varying compositions. And so the concentration dependence of the absorption intensity can be shown to follow predictions from this dimer model.

MO 17.6 Thu 12:30 PH/HS1

X-ray diffraction off isolated laser-aligned gas-phase molecules — •THOMAS KIERSPEL^{1,2}, FENGLIN WANG^{1,3}, and JOCHEN KÜPPER^{1,2,4} — ¹Center for Free-Electron Laser Science, DESY, Hamburg, Germany — ²The Hamburg Center for Ultrafast Imaging, University of Hamburg, Germany — ³PULSE Institute, Stanford University, Stanford, California, USA — ⁴Department of Physics, University of Hamburg, Germany

We report on x-ray diffraction off aligned isolated 2,5-diiodothiophene molecules. Using 0.13 nm (9.5 keV) radiation diffraction patterns were recorded at a degree of alignment of $\langle \cos^2 \theta \rangle \approx 0.85$. The short wavelength provides atomic resolution information of the molecular structure. The estimated 0.1 scattered photons/shot are mainly due to the two-center interference of the two iodines [1], with secondary signals due to the sulphur atom in the ring.

The main challenge of this experiment is the low signal-to-noise level. The experimental background is estimated to be more than 10 photons/shot, but should be largely discriminable due to photon energy differences. We discuss strategies on how to overcome the low signal-to-noise level and present resolutions by means of data analysis.

This work was carried out in a collaboration with spokespersons F. Wang, J. Küpper, P. Bucksbaum, and H. Chapman. The collaboration consists of CFEL, PULSE, LCLS, European XFEL, Aarhus University, Kansas State University, Stanford University, and Uppsala University. LCLS is operated by Stanford University on behalf of the US DOE.

[1] Küpper et al., *Phys. Rev. Lett.* **122**, 083002 (2014)

MO 17.7 Thu 12:45 PH/HS1

Precise study of deep two-body subradiance with ultracold Sr₂ molecules — •WOJCIECH SKOMOROWSKI^{1,3}, BART MCGUYER², MICKEY McDONALD², GEOFFREY IWATA², MARCO TARALLO², ROBERT MOSZYNSKI³, and TANYA ZELEVINSKY² — ¹Theoretische Physik, Universität Kassel, Heinrich-Plett-Str. 40, 34132 Kassel, Germany — ²Department of Physics, Columbia University, 538 West 120th Street, New York, NY 10027-5255, USA — ³Department of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland

Weakly bound molecules have physical properties without atomic analogues, even as the bond length approaches dissociation. For instance, the internal symmetries of homonuclear diatomic molecules result in the formation of two-body superradiant and subradiant excited states. While superradiance has been demonstrated in a variety of systems, subradiance is more elusive due to the inherently weak interaction with the environment. Here we directly probe deeply subradiant states in ultracold diatomic strontium molecules near the intercombination atomic line, and characterize their properties by *ab initio* model [1]. We find that two competing effects limit the lifetimes of the subradiant molecules, with different asymptotic behaviors. The first is radiative decay via magnetic-dipole and electric-quadrupole interactions. We prove that its rate grows quadratically with the bond length, confirming quantum mechanical predictions. The second is nonradiative decay through weak non-adiabatic predissociation, with a rate proportional to the vibrational spacing and sensitive to short-range physics.

[1] B. H. McGuyer et al., *Nat. Phys.* (2015), doi:10.1038/nphys3182.

MO 18: Biomolecules

Time: Thursday 11:00–13:00

Location: PH/SR106

Invited Talk

MO 18.1 Thu 11:00 PH/SR106

cis-trans Isomerization, Ion-Pumps and pH-Sensor: From Molecular Interactions to Biological Function — •ROLF DILLER¹, PATRICK SINGER¹, MIRIAM COLINDRES¹, PHILIPP ALT¹, EKKEHARD NEUHAUS², and TILMAN LAMPARTER³ — ¹TU Kaiserslautern, Germany — ²TU Kaiserslautern, Germany — ³KIT, Karlsruhe, Germany

Light sensing and photosynthesis are only the most prominent examples for quite many extremely important phenomena in biology that rely on photochemical reactions. In spite of their realization by a relatively small number of chromophores the great functional diversity is facilitated by fine tuned reaction control via balanced chromophore protein interaction. Besides their versatility in biology these systems can be used and adapted for artificial applications in medicine and biological research. This requires the detailed understanding of molecular processes on time scales from femtoseconds to seconds.

Here we focus on photoinduced cis-trans isomerization as fundamental reaction in retinal binding proteins (ion pumps, light sensing) and in bilin binding phytochromes (light sensing). Femtosecond time resolved UV/Vis and infrared vibrational spectroscopy is used to explore electronic and structural dynamics of the cofactor-protein moiety. We report on the ultrafast interaction of the isomerizing retinal chromophore with a water cluster in Bacteriorhodospin and on the biliverdin binding phytochrome Agp2 from *A. tumefaciens* that has been suggested to serve as light-based pH-sensor and exhibits unusual properties involving isomerization of the deprotonated chromophore.

MO 18.2 Thu 11:30 PH/SR106

Structure Determination of *trans*-Cinnamaldehyde using Broadband Microwave Spectroscopy — •SABRINA ZINN^{1,2,3}, THOMAS BETZ^{1,2,3}, and MELANIE SCHNELL^{1,2,3} — ¹Max Planck Institute for the Structure and Dynamics of Matter, Hamburg/Germany — ²Center for Free-Electron Laser Science, Hamburg/Germany — ³The Hamburg Centre for Ultrafast Imaging, Hamburg/Germany

The high-resolution rotational spectrum of gas-phase *trans*-cinnamaldehyde ((2E)-3-phenylprop-2-enal) has been obtained with

chirped-pulse microwave spectroscopy in the frequency range of 2 - 8.5 GHz. The odorant molecule is the essential component in cinnamon oil and causes the characteristic smell. Studying the structure of odorant molecules to learn more about the structure-odor relationship can give insights into molecular recognition by olfactory receptors.

We were able to assign the rotational spectra of *trans*-cinnamaldehyde as well as all single substituted ¹³C-species of the molecule. The change in mass, caused by carbon atom substitution in natural abundance, leads to a change of the molecular moments of inertia and thus of the rotational constants. From these additionally obtained parameters, the molecular structure can be determined by using for example Kraitchman's equations. The obtained structure can be used for a comparison to the structures of other odorant molecules.

MO 18.3 Thu 11:45 PH/SR106

IRMPD spectra of metal-lumiflavin ionic complexes — •ALAN GÜNTHER¹, PABLO NIETO¹, GIEL BERDEN², JOS OOMENS², JUDITH LANGER¹, and OTTO DOPFER¹ — ¹Institut für Optik und Atomare Physik, TU Berlin, Berlin, Germany — ²Radboud University Nijmegen, Institute for Molecules and Materials FELIX Facility, Nijmegen, The Netherlands

Flavins are a fundamental class of biomolecules with lumiflavin (LF) as its smallest member. They are involved in many important biological processes. For example, as a component of flavo-proteins, they participate in the repair of DNA [1]. To understand these phenomena at the molecular level, spectroscopic studies of the geometric and electronic structure of isolated flavins and their complexes are required. We report IRMPD spectra of mass-selected Me⁺-LF (Me = Li, Na, K, Cs, Cu, Ag) ionic complexes in the fingerprint range (800-1900 cm⁻¹) accompanied by DFT calculations. In solution, metal ions preferentially bind to N5 and O4 of the flavin [2]. In contrast, additional O2 binding sites are identified for all alkali metal ions in our experiments, whereas for Cs⁺ only the O2 position is observed. For Ag⁺ and Cu⁺ only O4 and N5 chelates are identified, although the presence of the O2 isomer cannot be excluded. These metals also bind with different angles compared to alkali metals due to covalent contributions caused by their electronic configuration. The limited spectral resolution of these ex-

periments will be overcome with our new apparatus equipped with a cryogenic 22-pole ion trap. [1] M. Sugiyama, EHP 92, 63 (1991); [2] P. Hemmerich and J. Lauterwein, Inorganic Biochemistry 1168 (1973)

MO 18.4 Thu 12:00 PH/SR106

Ultrafast coupling dynamics between the excited states of open chain carotenoids observed by fs time-resolved non-linear vibrational spectroscopy — •TAKESHI MIKI¹, RICHARD J. COGDELL², TIAGO BUCKUP¹, and MARCUS MOTZKUS¹ — ¹Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, D-69120 Heidelberg, Germany — ²Institute of Biomedicine & Life Science, University of Glasgow, G12 8QQ Glasgow, Lanark, Scotland

The ultrafast femtochemistry of carotenoids is governed by the interaction between electronic excited states. Electronic dark states of carotenoids and their interaction with optically active S2 state have been suggested to play a major role in the ultrafast deactivation of carotenoids and its properties. Here, we investigate this interaction between such dark and bright electronic excited states of open chain carotenoids, particularly its dependence on the number of conjugated double bonds (N). We focus on the ultrafast wave packet motion on the modified potential surface by the interaction between bright and dark electronic states. Pump-degenerate four-wave mixing (pump-DFWM) is applied to a series of carotenoids with different number of conjugated double bonds N = 9, 10, 11 and 13. Our results indicate that short carotenoids display strongly distorted potentials when compared to longer carotenoids. The magnitude of this anharmonicity can be explained by the efficient coupling between S2 and a dark Sx state (in this case a Bu type), which stabilizes the higher energy levels of the C-C and C=C vibrational modes at early delay times (T < 50 fs).

MO 18.5 Thu 12:15 PH/SR106

Enantiomer Identification of Mixtures of Chiral Molecules with Broadband Microwave Spectroscopy — •DAVID SCHMITZ¹, V. ALVIN SHUBERT¹, DAVID PATTERSON², JOHN M. DOYLE², and MELANIE SCHNELL¹ — ¹Max Planck Institute for the Structure and Dynamics of Matter at the Center for Free-Electron Laser Science, Hamburg, Germany — ²Department of Physics, Harvard University, Cambridge, MA, USA

Most molecules of biochemical relevance are chiral. Even though the physical properties of two enantiomers are nearly identical, they might exhibit completely different biological effects, e.g. one may be beneficial to health while the opposite is toxic. In nature and as products of chemical syntheses, chiral molecules often exist in mixtures with other chiral molecules. The analysis of these complex mixtures to identify the molecular components, determine which enantiomers are present, and to measure the enantiomeric excesses (ee) is still one of the challenging tasks of analytical chemistry.

We present here a new method of differentiating enantiomeric pairs of chiral molecules in the gas phase. It is based on broadband rotational spectroscopy and is a three-wave mixing process that involves a closed cycle of three rotational transitions. The phase of the acquired

signal bares the signature of the enantiomer, as it depends upon the product of the three transition dipole moments. Furthermore, this technique allows for determining of the ee, which is proportional to the signal amplitude. Our technique can be applied to mixtures of chiral molecules, even when the molecules are very similar.

MO 18.6 Thu 12:30 PH/SR106

Matter-wave interference enhanced metrology on biomolecules — •LUKAS MAIRHOFER, CHRISTIAN BRAND, PHILIPP GEYER, UGUR SEZER, LISA WÖRNER, and MARKUS ARNDT — Vienna University, Austria

Matter-wave interferometry is a powerful tool for the study of quantum properties of molecules (Berninger, PRA 76, 2007, Eibenberger, PRL 112, 2014). It has been demonstrated for up to 10.000 amu (Eibenberger, PCCP 15, 2013). As amplitude and phase of the fringe pattern are extremely sensitive to external forces matter-wave interference enhances the spatial resolution of deflectometry by a factor of 10e4 compared to ballistic deflectometry. This has been successfully conducted for electric deflection (Eibenberger, NJP 13, 2011).

Thus matter-wave interferometry enhanced deflectometry makes high precision measurements on complex biomolecules feasible. The determination of their magnetic, electric and optical properties allows the investigation of their structure, of photo-induced conformational changes and of photochemistry in the gas phase. Additional water-bonds mimic the molecule's natural environment and allow us to study the transition from gas-phase to in-vivo-behaviour. We will present a geometry for deflection in magnetic fields suitable for interferometry which requires a homogenous force over the extension of the beam. Furthermore we will introduce a source for beams of internally cold, neutral and intact biomolecules up to 4000 amu that are sufficiently slow and intense for interference experiments. Finally we will report on recent progress in our research on biomolecules.

MO 18.7 Thu 12:45 PH/SR106

Valence-Shell-Photoelectron Imaging of Controlled Biomolecules — •JOSS WIESE¹, SEBASTIAN TRIPPEL¹, and JOCHEN KÜPPER^{1,2,3} — ¹Center for Free-Electron Laser Science, DESY, Hamburg — ²The Hamburg Center for Ultrafast Imaging — ³Department of Physics, University of Hamburg

A molecule's chemical behaviour is governed by its electronic properties. Thus, a view at the evolution of the involved molecular orbitals during a reaction lures with insight into the fundamentals of chemistry.

In our experiments molecules are investigated by means of photoelectron imaging. State-selected molecular ensembles are laser aligned or mixed-field oriented inside a velocity map imaging spectrometer. The resulting velocity maps display the projected three dimensional distributions of both, the photoelectrons' kinetic energy and their release angle, in the molecular frame (MFPADs). MFPADs of various molecules will be discussed in terms of the molecular orbitals which are involved in the ionization process. Three dimensional MFPADs will be presented, which were obtained through tomographic reconstruction of the projected 2D images.

MO 19: Electronic Spectroscopy

Time: Thursday 14:30–16:15

Location: PH/HS1

Invited Talk

MO 19.1 Thu 14:30 PH/HS1

Luminescence properties of mass-selected lanthanoid complexes: a study involving gas-phase ion trapping, ion deposition into neon matrices, and computations. — •JEAN-FRANCOIS GREISCH¹, BASTIAN KERN², MICHAEL E. HARDING¹, JIŘÍ CHMELA², BERNHARD SCHÄFER¹, ARTUR BÖTTCHER², WIM KLOPPER^{1,2}, MARIO RUBEN^{1,3}, DETLEF SCHOSS^{1,2}, DMITRY STRELNIKOV², PATRICK WEIS², and MANFRED M. KAPPES^{1,2} — ¹Inst. of Nanotechnology, KIT (D) — ²Inst. of Physical Chemistry, KIT (D) — ³Inst. de Physique et Chimie des Matériaux, CNRS-Uni. Strasbourg (F)

Charged lanthanoid-antenna complexes are relevant to many fields, e.g., photovoltaics, light-emitting diodes, and quantum memories. Investigation of their excited state properties directly benefits from mass spectrometric methods since their luminescence is strongly affected by stoichiometry, symmetry, and overall charge state. The talk focuses on a comparison between the luminescence properties of mass-selected ions (i) isolated in solid cryogenic neon matrices and (ii) in a Paul trap.

For series of complexes having common stoichiometry but varied lanthanoid composition we observe vibrationally-resolved ligand-centered or lanthanoid-centered emission. Energy level shifts and splittings are rationalized in terms of structural changes, which were analyzed with the support of ion mobility measurements. The role of the ligand shell and the induced ligand field on the lanthanoid's energy levels, as well as the differences in the vibrationally resolved spectra, are interpreted with the support of density functional theory combined with Judd-Ofelt theory and Franck-Condon computations, respectively.

MO 19.2 Thu 15:00 PH/HS1

Exciton coupling in [AB](N) copolymers — •KLAUS RENZIEHAUSEN¹, CHRISTOPH LAMBERT², and VOLKER ENGEL¹ — ¹Institut für Physikalische und Theoretische Chemie, Emil-Fischer-Str. 42, Universität Würzburg, 97074 Würzburg, Germany — ²Institut für Organische Chemie, Universität Würzburg, Center for Nanosystems Chemistry, Am Hubland, 97074, Würzburg, Germany

In order to understand basic optical properties of alternating copoly-

mers we use exciton coupling theory in which the excited states of the polymers A and B. The mathematical description of the copolymers follows essentially the work of Kasha [1]. Within this model it is possible to explain the absorption lineshape of a squaraine-squaraine copolymer which was measured recently [2].

[1] Kasha, M. *Radiat. Res.* 20, 55-71 (1963)

[2] S. F. Völker, A. Schmiedel, M. Holzapfel, K. Renziehausen, V. Engel, *Ch. Lambert J. Phys. Chem. C* 118, 17467 (2014).

MO 19.3 Thu 15:15 PH/HS1

Geometry changes of ortho- and meta-Tolunitrile upon S1 -> S0 excitation: comparison of the effect of substituent positions in push-pull systems — ●FELIX GMEREK and MICHAEL SCHMITT — Heinrich-Heine-Universität, Düsseldorf, Germany

The nuclear structure of a molecule follows its electronic structure in the specific electronic state. Therefore, it is strongly influenced by electron pushing or pulling substituents and can easily be investigated by electronic spectroscopy.

Tolunitriles represent small push-pull-systems with an electron-pushing methyl-group and an electron-pulling cyano-group.

In this project, the ortho- and meta-isomers were investigated to compare the effects of different substituent positions.

According to the Franck-Condon-principle the fluorescence intensities depend on the geometry changes. Therefore the excited state geometry can be described by a displacement of the ground state, which is derived from the Franck-Condon-factors and the rotational constant changes.

The rotational constant changes upon electronic excitation have been measured by Alvarez-Valtierra et al. [1]. Additionally Franck-Condon-factors were obtained by single vibronic level fluorescence spectroscopy of the electronic origin and six vibronic bands for both isomers.

[1] personal communication

MO 19.4 Thu 15:30 PH/HS1

Non-Adiabatic Relaxation of Multi-Electronic Dynamics in Polycyclic Aromatic Hydrocarbons — ●MARTIN GALBRAITH¹, THOMAS BARILLOT², VICTOR DESPRE², JESSE KLEI¹, ALEXANDER KULEFF³, VINCENT LORiot², SUSANTA MAHAPATRA⁴, ALEXANDRE MARCINIAK², JOCHEN MIKOSCH¹, SAMALA NAGAPRASAD REDDY⁴, ARNAUD ROUZEE¹, CHRISTOPHER SMEENK¹, ALEXANDER TIELENS⁵, CHUNG-HSIN YANG¹, NICKOLAI ZHAVORONKOV¹, MARC VRAKING¹, and FRANCK LEPINE² — ¹Max-Born-Institut, Berlin, Germany — ²Institut Lumiere Matiere, Universite Lyon 1, Villeurbanne Cedex, France — ³Universitaet Heidelberg, Heidelberg, Germany — ⁴University of Hyderabad, Hyderabad, India — ⁵Leiden University, Leiden, The Netherlands

We present experimental evidence for an ultrafast relaxation mechanism that follows absorption of an XUV photon and is general for polycyclic aromatic hydrocarbons (PAH). Highly excited electronic states are created where electron correlation effects play a dominant role. The excitation of shake-up states by ionisation is followed by non-adiabatic relaxation dynamics on a time scale of 10s of fs. Various PAHs and their building block benzene have been studied with XUV pulses from

high-harmonic generation and an infrared probe pulse, leading to a time resolution down to sub-10 fs. The XUV-induced photochemistry of PAHs is of great interest in astrophysics due to their long-debated role in the origin of the diffuse interstellar bands. The satellite states in PAHs make these molecules interesting candidates for investigating attosecond hole migration following ionisation.

MO 19.5 Thu 15:45 PH/HS1

Determination of excited state dipole moments of various indole derivatives using rotationally resolved laser induced fluorescence spectroscopy — ●MARTIN WILKE¹, JOSEFIN WILKE¹, MICHAEL SCHMITT¹, and LEO MEERTS² — ¹Institute for Physical Chemistry I, Heinrich-Heine-University, Düsseldorf — ²Institute for Molecules and Materials, Radboud University, Nijmegen, The Netherlands

In solution the energetic order of the lowest excited singlet states of indole, called La and Lb in the nomenclature of Platt, depends dramatically on the polarity of the surrounding solvent. For the gas phase it could be shown that the energetic order can be influenced and even inverted by the insertion of differently acting substituents to the indole chromophore. High resolution laser induced fluorescence spectroscopy can be used to assign the electronic nature of excited singlet states from the orientation of the transition dipole moment or the magnitude of the permanent dipole moment of the electronically excited state. Therefore a homogeneous static electric field is created, which lifts the M degeneracy by the Stark effect and results in a band splitting depending on the intensity of the electric field and on the order of the dipole moment in the ground and in the excited state. The Stark spectra of several indole derivatives have been measured and analyzed using an evolutionary algorithm. Thereby the nature of the excited state can be discussed by means of its dipole moments.

MO 19.6 Thu 16:00 PH/HS1

Single Molecule Magnets investigated by gas phase X-ray Magnetic Circular Dichroism (XMCD) spectroscopy — ●MATTHIAS TOMBERS¹, JOACHIM HEWER¹, JONATHAN MEYER¹, GEREON NIEDNER-SCHATTEBURG¹, and TOBIAS LAU² — ¹Fachbereich Chemie & Forschungszentrum OPTIMAS, Technische Universität Kaiserslautern, Kaiserslautern, Germany — ²Helmholtz-Zentrum Berlin für Materialien und Energie, BESSY II, Berlin, Germany

We have recorded the first XMCD spectra of different isolated Single Molecule Magnets (SMMs) in the gas phase to deduce their intrinsic magnetic properties void of any surface or packing effects. We report the XMCD spectrum of the archetypal SMM Mn12-acetate on the Mn L3,2 absorption edges. Furthermore, we recorded the XMCD spectra of different [Fe4Ln2Lx]-type SMMs (Ln=Gd, Tb, Dy; L = different organic ligands) on the Fe L3,2- and the Ln M5,4- absorption edges respectively. The element selectivity of the XMCD technique allows us to determine the contribution of the different metals to the total magnetic moment of the molecules. Furthermore, sum rule analysis of the recorded XMCD spectra allows us to separate the total magnetic moment into its spin and orbital contribution. We have performed InfraRed Multi Photon Dissociation (IRMPD) spectroscopy of these molecules to address those magnetic moments to their structural features.

MO 20: Theory: Molecular Dynamics

Time: Thursday 14:30–16:45

Location: PH/SR106

Invited Talk

MO 20.1 Thu 14:30 PH/SR106

Controlling charge migration in molecules — ●ALEXANDER I. KULEFF — Theoretische Chemie, PCI, Universität Heidelberg

Exposing molecules to ultrashort laser pulses can trigger pure electron dynamics in the excited or ionized system. In the case of ionization, these dynamics may manifest as an ultrafast migration of the initially created hole-charge throughout the ionized molecule and were termed *charge migration* [1]. Charge migration is solely driven by electron correlation and appeared to be a rich phenomenon with many facets that are rather characteristic of the molecule studied [2]. All this increasingly attracts the attention of the scientific community from both theoretical and experimental sides. Due to the coupling between the electronic and the nuclear motion, the control over the pure electron dynamics offers the extremely interesting possibility to steer the suc-

ceeding chemical reactivity by predetermining the reaction outcome at a very early stage. A way to control the charge migration by appropriately tailored [3] femtosecond laser pulses will be presented and the consequences of such a scheme will be discussed.

[1] L. S. Cederbaum and J. Zobeley, *Chem. Phys. Lett.* **307**, 205 (1999).

[2] A. I. Kuleff and L. S. Cederbaum, *J. Phys. B* **47**, 124002 (2014).

[3] N. V. Golubev and A. I. Kuleff, *Phys. Rev. A* **90**, 035401 (2014).

MO 20.2 Thu 15:00 PH/SR106

Dynamics of H₂⁺ in intense laser fields: Full-dimensional approximate quantum-mechanical description of dissociation and ionization — ●TOBIAS FIEDLSCHUSTER, JAN HANDT, FRANK GROSSMANN, and RÜDIGER SCHMIDT — Technische Universität Dresden

So far, even for nature's simplest molecule H_2^+ , no exact quantum-mechanical description of the laser-induced dynamics (i. e., simultaneously including vibration, rotation, dissociation and ionization) has been achieved.

In this work, we present a full-dimensional approximate quantum-mechanical treatment. It is based on the extension of a recently developed ab-initio Born-Oppenheimer surface hopping approach (M. Fischer, J. Handt and R. Schmidt, Phys.Rev. A 90, 012525 (2014), ibid 012526, ibid 012527) to hopping between Floquet surfaces.

The obtained results for dissociation and ionization are in very good agreement with recent experimental data (J. McKenna et al., Phys. Rev. A 85, 023405 (2012)).

The extension of the method to many-electron molecules is discussed.

MO 20.3 Thu 15:15 PH/SR106

Influence of vibrations on the energy transfer in Fenna-Matthews-Olson complex — ●XIAOMENG LIU and OLIVER KÜHN — Institut für Physik, Universität Rostock, D-18051, Germany

We have numerically calculated the effect of vibrational modes on the exciton quantum coherence and energy transfer dynamics of the FMO complex, employing the experimental spectral density from Ref. [1]. The exciton Hamiltonian is restricted to the single excitation space of the seven site FMO model [2]. Particular emphasis is laid on the way, explicit vibrational motions are included. Here, one- (OPA) and two-particle approximations (TPA) are compared. The dynamics is analyzed by means of a Markovian quantum master equation [3]. We examined the influence of vibrations on the populations and coherences, for different values of the Huang-Rhys factor and the temperature. We found that decoherence and equilibration is faster in the TPA, where vibrational motion in the electronic ground state is included.

[1] Wendling, M. et al., J. Phys. Chem. B **104**, 5825(2000)

[2] Schmidt am Busch, M. et al., J. Phys. Chem. **2**, 93(2011)

[3] Kühn, O. et al., Chem. Phys. **204**, 99(1996)

MO 20.4 Thu 15:30 PH/SR106

Transition state spectroscopy of the [H,C,N] molecular system — ●GEORG CH. MELLAU^{1,2}, ROBERT W. FIELD², OLEG L. POLYANSKY^{3,4}, and ALEXANDRA A. KYUBERIS⁴ — ¹Physikalisch-Chemisches Institut, Justus-Liebig-Universität Giessen, Germany — ²Department of Chemistry, MIT, Cambridge, MA, USA — ³Department of Physics and Astronomy, University College London, Gower St, London, UK — ⁴Institute of Applied Physics, Russian Academy of Science, 46 Uljanov Street, Nizhny Novgorod, Russia

In this work we study the molecular eigenstates at the transition state of the HCN \leftrightarrow HNC isomerization using our set of vibrationally assigned ab initio rovibrational eigenenergies. As the vibrational excitation energy approaches the isomerization barrier, the eigenstates show a vibrational angular momentum dependent Dixon-dip like trend [1], which correlates with the semiclassical pattern of the level spacings [2]. Based on this analysis, we can determine the proximity of an eigenstate to the effective isomerization barrier. The barrier proximal "saddle point states" are found to be highly localized in the bending coordinate at the saddle point. Our picture explains why the localization takes place not only for pure bending states but also at higher energies, exactly when the eigenenergies match the effective barrier height corresponding to the extra energy in the excited stretch. Saddle point localized states have been reported in [3]. [1] G. Ch. Mellau, J. Chem. Phys. **133**, 7164303 (2010) [2] J. Baraban et al., in prep. (2014) [3] J. R. Henderson et al. J. Chem. Soc. Faraday Trans. **88**, 328 (1992)

MO 20.5 Thu 15:45 PH/SR106

Evolving classical nuclei on a single time-dependent potential in electronic non-adiabatic processes — ●FEDERICA AGOSTINI¹, ALI ABEDI², YASUMITSU SUZUKI³, SEUNG KYU MIN¹, NEEPA T. MAITRA², and EBERHARD K. U. GROSS¹ — ¹Max-Planck-Institute of Microstructure Physics, Halle, Germany — ²Department of Physics and Astronomy, Hunter College and the Graduate Center of the City University of New York, USA — ³National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan

The Born-Oppenheimer (BO) approximation allows us to visualize dynamical processes in molecular systems as a set of nuclei moving on a single potential energy surface representing the effect of the electrons in a given eigenstate. Yet, this is an approximation, and many interesting phenomena, such as vision or Joule heating in molecular junctions, take place in conditions beyond its range of validity. Nevertheless, the basic construct of the adiabatic treatment, the BO potentials, is

employed to describe non-adiabatic processes, as the full problem is represented in terms of adiabatic states and transitions among them in regions of strong non-adiabatic coupling. But the concept of single potential energy is lost. An alternative point of view will be presented: a single, time-dependent, potential [1] arises from the exact factorization of the electron-nuclear wave function, providing the force [2, 3] that drives nuclear motion, also in non-adiabatic situations. [1] Abedi et al., PRL **110** 263001 (2013); [2] Agostini et al., Mol. Phys. **111** 3625 (2013); Agostini et al., arXiv:1406.4667 [physics.chem-ph] (2014); [3] Abedi et al., EPL **106** 33001 (2014); Agostini et al., accepted JCP (2014).

MO 20.6 Thu 16:00 PH/SR106

On-the-fly Parametrisation of the Frenkel Exciton Hamiltonian — ●PER-ARNO PLÖTZ and OLIVER KÜHN — Universität Rostock, D-18051, Germany

Electronic Excitation Energy transfer in molecular aggregates can be described by the Frenkel exciton approach [1]. Here the problem is separated into local transitions interacting via Coulomb Coupling. The presence of thermal fluctuations implies statistic sampling of these parameters. In a condensed phase this requires to take into account not only intramolecular vibrations and deformations but also solvent contributions.

An efficient method enabling such a description of molecular dynamics and energy transfer on the same footing is density-functional based tight-binding (DFTB). In this contribution we present the recently developed Tight-Binding-Frenkel-Exciton (TBFE) approach [2] and apply it to aggregates of chromophores like porphyrins or perylenes in different environments. This efficient method can provide the input for simulations of exciton dynamics spectroscopy.

[1] V. May and O. Kühn. *Charge and Energy Transfer Dynamics in Molecular Systems* (Wiley-VCH, Weinheim 2011)

[2] P.-A. Plötz, T. Niehaus, O.Kühn, J. Chem. Phys. **140**, 174101 (2014)

MO 20.7 Thu 16:15 PH/SR106

Ultrafast Energy Transfer from Solvent to Solute induced by Sub-picosecond Highly Intense THz Pulses — ●PANKAJ KR. MISHRA^{1,2,3}, ORIOL VENDRELL^{1,3}, and ROBIN SANTRA^{1,2,3} — ¹Center for Free-Electron Laser Science, DESY, Hamburg, Germany — ²Department of Physics, University of Hamburg, Germany — ³Center for Ultrafast Imaging, University of Hamburg, Germany

Liquid water is the single most important medium in which chemical and biological processes take place. The possibility to generate sub-ps and very intense THz pulses at free-electron lasers in full synchronization with the X-rays (XFEL) opens the possibility to time-resolved investigations of transient state of water and of molecular species dissolved in it. At low intensity, THz light couples to low energy collective modes of the liquid. Here, we investigated the response of liquid water to one and half cycle, 200 fs long THz pulses spectrally centered at about 100/cm (3 THz). The pulse with an intensity of about $5 \cdot 10^{12}$ W/cm² transfers the energy mostly to the translational and rotational modes of the water monomers in a small time-scale when the pulse is about to reach its peak. The intramolecular vibrational energy also follows them after tens of fs during the pulse. Water reaches to a quasi-equilibrium state which is gas like very hot liquid. We also investigated the response of Phenol molecule to such THz pulse in vapor phase and in liquid water environment. Here the single phenol doesn't gain energy due to such pump pulse. But the phenol in liquid water gains significant amount of energy due to strong collision of highly mobile water molecule.

MO 20.8 Thu 16:30 PH/SR106

Auger electron spectroscopy of liquid water: The role of intermolecular electronic relaxation and proton transfer — ●NIKOLAI V. KRYZHEVOI¹, PETR SLAVÍČEK², BERND WINTER³, and LORENZ S. CEDERBAUM¹ — ¹Theoretical Chemistry, University of Heidelberg, Germany — ²Department of Physical Chemistry, Institute of Chemical Technology, Prague, Czech Republic — ³Joint Laboratory for Ultrafast Dynamics in Solutions and at Interfaces, Helmholtz-Zentrum Berlin, Germany

Electronic relaxation of core-ionized water molecules in liquid is far more diverse and complex than anticipated, and extremely different from that in an isolated water molecule. This has been revealed by simulating Auger electron spectra of normal and heavy liquid water using ab initio and quantum dynamical methods and comparing the theoretical results with the available experimental data [1]. A core-ionized

water molecule in the liquid phase, in addition to a local Auger process, relaxes through non-local energy- and charge-transfer, such as Intermolecular Coulombic Decay (ICD) [2] and Electron Transfer Mediated Decay (ETMD) [3]. These intermolecular decay processes play a surprisingly important role, especially ETMD which is considered for the first time in the core-level regime. The electronic relaxation is accompanied by ultrafast proton transfer dynamics [4] which enhances the efficiency of the non-local processes considerably. As a consequence, the double charge forming in the end of the electronic and nuclear relaxation tends to be distributed between different water monomers

rather than be localized on a single molecular unit and various reactive oxygen species are created. Our study provides insight into the types and yields of these species. [1] P. Slavíček, B. Winter, L.S. Cederbaum, N.V. Kryzhevoi, J. Am. Chem. Soc. doi: 10.1021/ja5117588. [2] L.S. Cederbaum, J. Zobeley, F. Tarantelli, Phys. Rev. Lett. 79, 4778 (1997). [3] J. Zobeley, R. Santra, L.S. Cederbaum, J. Chem. Phys. 115, 5076 (2001). [4] S. Thürmer, M. Ončák, N. Ottosson, R. Seidel, U. Hergenahn, S.E. Bradforth, P. Slavíček, B. Winter, Nature Chem. 5, 590 (2013).

MO 21: Posters 4: Novelties in Molecular Physics

Time: Thursday 17:00–19:00

Location: C/Foyer

MO 21.1 Thu 17:00 C/Foyer

Toward spectroscopy with PAH and fullerene ions in a cryogenic trap — •JÜRGEN GÖCK¹, KLAUS BLAUM¹, CHRISTIAN BREITENFELDT², ULRICH GRÖZINGER³, THOMAS HENNING³, JONAS KARTHEIN¹, BASTIAN KERN⁴, SUNIL KUMAR S.¹, CHRISTIAN MEYER¹, GAËL ROUILLE³, DMITRY STRELNIKOV⁴, ANDREAS WOLF¹, SEBASTIAN GEORGE¹, and HOLGER KRECKEL¹ — ¹Max-Planck-Institut für Kernphysik, Saupfercheckweg 1, 69117 Heidelberg, Germany — ²Institut für Physik, Ernst-Moritz-Arndt-Universität Greifswald, Felix-Hausdorff-Straße 6, 17487 Greifswald, Germany — ³Max-Planck-Institut für Astronomie, Königstuhl 17, 69117 Heidelberg, Germany — ⁴Institut für Physikalische Chemie II, Karlsruher Institut für Technologie, Kaiserstraße 12, 76131 Karlsruhe

Gas phase spectroscopy with large molecular ions is still a challenging subject. We are currently developing a novel technique which is based on sensitive detection of mid-infrared photons. For this we use the Cryogenic Trap for Fast ion beams (CTF) [1], which reflects the ions back and forth between two electrostatic mirrors. Einzel lenses focus the ion beam toward the trap center. The cryogenic temperature of the environment (<15 K) leads to residual-gas densities of 2000 particles/cm³, corresponding to a pressure of $\sim 10^{-13}$ mbar at room temperature, and an almost black-body radiation free background. We will present the details about the available ion source and the ion optics used for the injection of the ions into the trap. The measurement principle and the experimental program will be discussed.

[1] M. Lange et al., Rev. Sci. Instrum. 81 (2010) 055105.

MO 21.2 Thu 17:00 C/Foyer

Structural rearrangement by an IR excitation in isolated hydroxychromones — •ANKE STAMM, MARTIN WEILER, KIRSTEN SCHWING, and MARKUS GERHARDS — TU Kaiserslautern, Fachbereich Chemie, Physikalische und Theoretische Chemie, Erwin-Schrödinger-Straße 52, 67663 Kaiserslautern

Photochemical reactions as the excited state proton transfer are of great interest due to their importance in chemical and biological processes. Molecular beam investigations combined with double, triple and quadruple resonance IR/UV spectroscopic techniques are very powerful tools to analyze structures and photochemically induced reactions. In comparison with (TD)-DFT calculations direct structural information on the electronic ground and electronically excited state of isolated molecules and clusters are obtained. Here we present studies on the photochemically reactive 3-hydroxychromone and 3-hydroxyflavone as well as clusters with water. In order to analyze structures and proton transfer reactions of different isomers/species with overlapping UV transitions in different electronic states, the quadruple resonance methods yield unambiguous results. Furthermore in a new approach for neutral isolated clusters IR/IR/UV/UV spectra indicate that the first IR excitation can lead to a rearrangement reaction of a cluster which is analyzed by the second IR excitation in combination with a resonant two photon ionization.

MO 21.3 Thu 17:00 C/Foyer

Collinear two-dimensional spectroscopy with shot-to-shot phase cycling — •SEBASTIAN ROEDING¹, SIMON DRAEGER¹, ANDREAS STEINBACHER¹, PATRICK NUERNBERGER^{1,2}, and TOBIAS BRIXNER¹ — ¹Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg — ²Physikalische Chemie II, Ruhr-Universität Bochum, 44780 Bochum

Experimental setups to perform two-dimensional electronic spec-

troscopy are typically based on coherently emitted optical signals in the phase-matching direction [1]. In contrast, the detection of incoherent signals allows the investigation of molecules in different environments, e.g. by fluorescence detection in the liquid phase [2] or by photocurrent measurement in the solid state [3]. In order to discriminate the different signal contributions phase-cycling [4] needs to be applied.

We introduce a novel setup which utilizes an AOPDF pulse shaper (Dazzler, Fastlite) to generate multi-pulse sequences in a collinear beam arrangement. The AOPDF allows the variation of the interpulse delays and their relative phases with 1 kHz rate, enabling a rapid scan and shot-to-shot phase cycling. The pulse shaper output can be guided to separate experiments which permits the investigation of molecules in different environments.

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

[2] Tekavec et al., J. Chem. Phys. 127, 214307 (2007)

[3] Aeschlimann et al., Science 333, 6050 (2011)

[4] Tian et al., Science 300, 1553 (2003)

MO 21.4 Thu 17:00 C/Foyer

Ultrafast studies on luminescent dinuclear copper(I) complexes in solid and liquid phase — •FLORIAN BÄPPLER¹, PATRICK SINGER¹, FABIAN RUPP¹, FLORIAN LIEDY¹, BENEDIKT BURGARD¹, DANIEL VOLZ², STEFAN BRÄSE³, and ROLF DILLER¹ — ¹Dept. of Physics, TU Kaiserslautern, 67663 Kaiserslautern, Germany — ²cynora GmbH, 76646 Bruchsal, Germany — ³Inst. of Organic Chemistry, KIT, 76131 Karlsruhe, Germany

Luminescent dinuclear copper complexes are very promising candidates as emitters in organic light-emitting diodes (OLEDs), as they combine high efficiencies, a widely tuneable emission maximum and low cost. However, further investigation of the primary photophysics and photochemistry is needed to fully understand important effects such as quenching mechanisms, especially in solid state. We present the first femtosecond (fs) transient reflectivity measurements on a dinuclear copper(I) complex Cu₂I₂MePyRPHOS[1] in solid state, under varied conditions, such as temperature and sample environment (air, vacuum), alongside with fs-transient absorption measurements in solution [2]. A comparison of the results reveals both similarities and differences between the photophysics in solid and liquid state which are critically discussed.

[1] D. Volz, D. M. Zink, T. Bockrocker, J. Friedrichs, M. Nieger, T. Baumann, U. Lemmer, S. Bräse, Chem. Mater. 2013, 25, 3414-3426

[2] D. Imanbaev, Y. Nosenko, C. Kerner, K. Chevalier, F. Rupp, C. Riehn, W.R. Thiel, R. Diller, Chemical Physics 442 (2014) 53-61

MO 21.5 Thu 17:00 C/Foyer

Excitonic spectral diffusion investigated by collinear 2D-VIS spectroscopy — •MERLE OHLSEN, STEFFEN WOLTER, FRANZISKA FENNEL, and STEFAN LOCHBRUNNER — Institut für Physik, Universität Rostock, 18051 Rostock

Large exciton diffusion lengths are desirable for many organic optoelectronic applications like solar cells. However, the migration distance is often limited by trapping of the excitons due to energetic disorder. A model system consisting of a polymer matrix doped with the perylene bisimide dye Perylene Red has proven to be suitable to investigate the influence of energetic disorder on the mobility of the excitons since its system parameters controlling the relevant processes are well understood [1]. It was shown, that the exciton dynamics in these films are determined by dispersive energy migration on the picosecond timescale. The dynamics can be described by a model based on Förster theory that takes inhomogeneous broadening and energetic disorder of the

donor and acceptor states into account [1]. To study the influence of the donor energy on the migration steps, we now focus on the dependence of the dynamics on the optical excitation frequency. To this end a newly implemented collinear 2D-VIS spectrometer based on a pulse shaper is applied. This allows for femtosecond absorption measurements with a site-selective excitation within the inhomogeneously broadened energetic distribution of the Perylene Red molecules.

[1] Fennel F., Lochbrunner, S., *Phys. Rev. B*, **85**, 094203 (2012)

MO 21.6 Thu 17:00 C/Foyer

Channel-Resolved Electron Recollision in Polyatomic Molecules — ●JOCHEN MIKOSCH, SASCHA BIRKNER, FEDERICO FURCH, ALEXANDRIA ANDERSON, CLAUS PETER SCHULZ, and MARC J. J. VRAKKING — Max-Born-Institut, Berlin, Germany

The emerging strong laser field driven spectroscopies promise to bring unprecedented time- and spatial resolution to atomic and molecular dynamics studies. It has become clear in recent years that a number of the initial simplifying assumptions, such as the adiabatic and the single-electron approximation, can break down and have to be replaced by a multi-electron picture. In particular the appearance of multiple ionization continua in Strong-Field Ionization and High Harmonic Generation of polyatomic molecules is being increasingly investigated theoretically and experimentally. Employing laser-aligned hydrocarbon molecules in a reaction microscope, we are studying how multiple strong-field ionization continua manifest themselves in electron recollision, driven by the strong laser field. Electron diffraction patterns for different fragments promise to characterize ionization channel resolved continuum electron wavepackets, emerging from different Dyson orbitals. This might evolve into an ultrafast dynamical probe of electronic coherences in molecules.

MO 21.7 Thu 17:00 C/Foyer

Realization of ultrafast time resolved spectroscopy using a Kretschmann arrangement — ●ALIREZA MAZAHERI TEHRANI, FAEZEH MOHAGHEGH, and ARNULF MATERNY — Jacobs University, Campus Ring 1, 28759 Bremen, Germany

The interactions of molecules adsorbed on thin metal films with surface plasmon polaritons are of great importance for spectroscopic applications, such as surface enhanced Raman spectroscopy (SERS). So far, experimental SERS investigations have mostly been performed in the frequency domain using continuous wave lasers. This way, although the results are quite interesting concerning applications, they mostly fail to nicely address the underlying physical concepts and mechanism of SERS. Time-resolved experiments, however, would help us to gain a better understanding of the underlying energy transfer mechanisms between electronic systems of metal and adsorbate due to their different time scale characteristics. In order to study the interaction in a reproducible manner, we use a Kretschmann configuration setup, through which surface plasmons were excited with femtosecond laser pulses (Pump) adjusted to the ground state absorption. Dynamic information of the system, could then be probed by another time-delayed femtosecond laser pulse, which could freely be adjusted to other excited states of adsorbates or to the ground state absorption. This experiment provides us with a much deeper insight into the energy transfer mechanisms between SPPs and molecules. In our contribution, we will present and discuss the time-resolved results.

MO 21.8 Thu 17:00 C/Foyer

Ultrafast Dynamics of Azobenzene-Polymers — ●ELENA PAVLENKO and MATIAS BARGHEER — Potsdam University, Germany

The general mechanism of excitation and relaxation in Azobenzene molecules has been a great interest for ultrafast dynamics and now is well understood. Although this molecule was mainly investigated in the liquid phase, few experiments in polymers were reported. We investigate the structural dynamics of the Azobenzene-containing polyelectrolyte multilayer structure PAzo/PAH. The samples are prepared by layer-by-layer deposition, which allows a lateral structuring of the polymer with photoactive species on the nanometer lengthscale. Polished quartz discs are used as the substrate which are surface-modified by adsorption of a PEI layer. Multilayers of PAzo and PAH with different structures are investigated. The sample was excited from the polymer side with 400nm light (1.4 mJ/cm²), in order to stimulate Azobenzene. Due to the electronic excitation, Azobenzene molecules can switch their isomerization state. This structural motion leads to a pronounced expansion of the layer on an ultrafast timescale. We analyze the hypersound-wave created by this expansion by broadband time-domain Brillouin scattering. The photoexcitation leads to a tran-

sient change of the complex refractive index. The transient absorption change due to the electronic excitation gives access to the imaginary part. The transient reflection change allows us to observe an optical contraction of the layer, which can be explained by two contributing effects: physical expansion and an even stronger reduction of the real part of the refractive index.

MO 21.9 Thu 17:00 C/Foyer

Spectroscopic tracking of the primary visual event — ●JONG MIN LIM, ALEX S DUARTE, GIOVANNI BASSOLINO, CHRISTOPH SCHNEIDERMAN, TORSTEN WENDE, and PHILIPP KUKURA — Physical & Theoretical Chemistry Laboratory, University of Oxford, South Parks Road, Oxford, OX1 3QZ, United Kingdom

The excited-state properties and kinetics of molecules can be extracted from ultrafast time-resolved electronic absorption or emission spectroscopy. It remains experimentally challenging, however, to obtain detailed information about the underlying structural and electronic changes immediately (<50 fs) after photon absorption, during which some of the most dramatic changes occur. To address these shortcomings, we have developed an ultra-sensitive transient absorption setup capable of simultaneously producing sub-10 fs pump pulses in the visible and dump pulses in the near-IR spectral region. We illustrate the benefits of such an approach by investigating the 11-cis to all-trans photoisomerization of rhodopsin and its chromophore in solution. We track transient absorption signal changes at long time-delays in the photoproduct spectral region as a function of pump-dump delay. Such measurements do not suffer from coherent artifact contributions commonly encountered in transient absorption and allow us to obtain critical information about the earliest dynamics of the system.

MO 21.10 Thu 17:00 C/Foyer

Single Molecule Localisation Microscopy of the Distribution of Chromatin Nanostructures Using Hoechst and Dapi Fluorescent Probes — ●UDO BIRK^{1,2,3}, ALEKSANDER SZCZUREK¹, KIRTI PRAKASH¹, HYUN-KEUN LEE^{1,3}, DOMINIKA ZUREK-BIESIADA⁴, GERIT BEST², MARTIN HAGMANN², JUREK DOBRUCKI⁴, and CHRISTOPH CREMER^{1,2,3} — ¹Institute of Molecular Biology, Mainz, Germany — ²Heidelberg University, Germany — ³Institut für Physik, Mainz University, Germany — ⁴Jagiellonian University, Kraków, Poland

We present a Single Molecule Localization Microscopy application of specific fluorescent DNA dyes such as DAPI, Hoechst and others, in order to obtain chromatin/nuclear DNA density maps with high optical and structural resolution. The approach adopted here is based on photoconversion to the green-emitting form of these dyes that later may undergo a process of switching under high intensity blue light. In mammalian cell nuclei, this technique yielded a single molecule localization precision in the order of 15 - 30 nm, corresponding to an optical (two-point) resolution of roughly 40 - 70 nm. We investigated various DNA structures and obtained data with a DNA-bound fluorophore density as high as 5000 SM/micrometer², significantly higher than previously reported.

[1] A. Szczurek et al. Nucleus 2014.

MO 21.11 Thu 17:00 C/Foyer

Ion molecule reaction dynamics of two center hydrocarbons — EDUARDO CARRASCOSA¹, ●JENNIFER MEYER¹, FREDRIK LINDÉN², MARTIN STEI¹, MARTIN BAWART¹, FABIO CARELLI¹, WOLF DIETRICH GEPPERT², and ROLAND WESTER¹ — ¹Institute for Ion Physics and Applied Physics, University of Innsbruck, 6020 Innsbruck, Austria — ²Department of Physics, Stockholm University, Stockholm, Sweden

We present recent results on the studies of the bimolecular substitution (S_N2) reactions of halogenated hydrocarbons. These reactions feature rich dynamics and product distributions [1]. The reaction dynamics were recorded with our crossed beam velocity map imaging (VMI) spectrometer [2]. The studied model systems include the reactions of fluoride anions F⁻ with methylchloride CH₃Cl which allows us to study the effect which the leaving group has on the reaction dynamics and product distribution. Moreover using CN⁻ as a nucleophile, we are able to study of isomer selective reaction channels. In the future, the ongoing work on the S_N2 reactions of methylhalides will be extended to ethylhalide molecules. If the carbon chain is extended, the substitution reaction S_N2 will be in competition with the elimination reaction E2. The dynamics and energy dependence of this competition of S_N2 and E2 will be studied.

[1] J. Xie, R. Otto, J. Mikosch, J. Zhang, R. Wester, W. L. Hase, *Acc. Chem. Res.*, **47**, 2960 (2014) [2] R. Wester, *PCCP*, **16**, 396 (2014)

MO 21.12 Thu 17:00 C/Foyer

Signatures of Interatomic-Coulombic-Decay in electron-impact ionization of argon dimers — ●THOMAS PFLÜGER¹, XUEGUANG REN¹, and ALEXANDER DORN² — ¹Physikalisch-Technische Bundesanstalt, Bundesallee 100, 38116 Braunschweig — ²Max-Planck-Institut für Kernphysik, Saupfercheckweg 1, 69117 Heidelberg

After decades of investigation of the ionization dynamics of simple atoms and molecules in electron collision experiments, in recent years significant progress was being made. The investigation of small rare gas clusters presents a unique opportunity in atomic physics. In a sense they can be thought of as bridging the gap between sole constituents and macroscopic matter, while still being simple enough to be understood on a particle level. For example, interesting processes were discovered in dimers such as Interatomic-Coulombic-Decay (ICD), which have been found to occur on very short time scales with a high efficiency compared to other possible pathways.

We find signatures of ICD in the triply-charged final-state of Ar₂, as well as interesting structure in the kinetic-energy-release spectrum of the doubly-charged final-state of Ar₂ pointing towards two separate mechanisms: a fast and a delayed one. Furthermore, a significant amount of data for the dissociation of Ar₃ → Ar₂⁺ + Ar⁺ could be retrieved.

Electronic as well as ionic energy spectra and angular distributions will be presented.

MO 21.13 Thu 17:00 C/Foyer

High resolution spectroscopy on LiSr — ●ERIK SCHWANKE¹, ASEN PASHOV², ALEXANDER STEIN¹, HORST KNÖCKEL¹, and EBERHARD TIEMANN¹ — ¹QUEST und Inst. f. Quantenoptik, Leibniz Universität Hannover — ²Department of Physics, Sofia University, Sofia, Bulgaria

The mixed alkali-alkaline earth molecules have recently attracted the interest of the scientific community due to possible applications in the field of cold and ultracold molecules. The combination of alkaline and alkaline earth atoms leads to molecules which have permanent electric and magnetic dipole moments and thus offer manipulation of their states by external fields. Several ab initio calculations have been published on atomic combinations like LiCa, LiSr or RbSr by various groups, reflecting the high interest by experimentalists. Experimentally, not so much is known about molecular electronic states. Up to now the ground state and two electronically excited states of LiCa and few states of LiBa have been characterised. We have successfully recorded the near infrared spectrum of LiSr. The molecules were created in a three section-heatpipe with different temperatures, this way accounting for the different vapour pressures. The thermal emission was dispersed by a high resolution Fourier transform spectrometer. The assignment of the dense spectrum was made possible by shining a diode laser tuned to a molecular line into the sample. This approach allowed to find and assign those transitions connected with the laser excitation. A first assignment of lines will allow predictions for further measurements. We will report the status of the investigations.

MO 21.14 Thu 17:00 C/Foyer

Towards THz + IR action spectroscopy of charged water clusters in a cryogenic multipole ion trap — ●STEFFEN SPIELER, SUNIL KUMAR, SEUNGHYUN LEE, ERIC ENDRES, DANIEL HAUSER, OLGA LAKHMANSKAYA, TIM MICHAELSEN, and ROLAND WESTER — Institute for Ion Physics and Applied Physics, University of Innsbruck, 6020 Innsbruck, Austria

Driving rovibrational transitions by continuous THz radiation in size selected and cryogenically cooled water clusters or macromolecules is a promising approach to unravel the structure and dynamics of weakly bound systems. It will allow to investigate long range interactions that are of fundamental interest for physics, chemistry and in life science. For experiments on intramolecular vibrational relaxation of biomolecules upon UV excitation or rotational transitions in OH⁻(H₂O)_n and H₃O⁺(H₂O)_n a THz radiation source based on difference frequency mixing of two near infrared diode lasers was set up as well as a versatile ion trap based experiment including an electrospray ion source, which can be used to generate intact macromolecular ions (positive/negative) in gas-phase. Ions generated in the electrospray ion source are focused and guided by means of an ion funnel and a quadrupole ion guide. Furthermore, the ions are mass selected by a quadrupole mass filter and loaded into a 16-pole radiofrequency ion trap. Benchmark THz action spectroscopy experiments on cold hy-

droxyl anions were performed, proving the applicability of difference frequency mixing based terahertz spectroscopy in an ion trap.

MO 21.15 Thu 17:00 C/Foyer

Towards Imaging of cold Penning-Reactions using a Li-MOT — ●JONAS GRZESIAK, HANNA MAIER, FRANK STIENKEMEIER, and MARCEL MUDRICH — Physikalisches Institut, Uni Freiburg, Hermann-Herder-Str 3, 79104 Freiburg i.Br.

Recent developments in merged beams have shed new light on cold reactive scattering.[1] Our setup for elastic scattering of cold molecular beam atoms originating from a rotating nozzle and Li-atoms in a MOT is extended for reactive scattering. To this end a supersonic and cryogenic pulsed nozzle with a home-made dielectric barrier discharge has been constructed which provides an intense and cold beam of metastable atoms. We show first results on cold penning reactions of the pulsed beam atoms with the rotating nozzle beam atoms, as well as reactions between ultracold Li-atoms originating from the MOT and the pulsed beam atoms. In prospect of imaging the reaction kinematics the use of an ion imaging detector is discussed.

[1] A. B. Henson, S. Gersten, Y. Shagam, J. Narevicius, E. Narevicius, Science 338, 234 (2012).

MO 21.16 Thu 17:00 C/Foyer

Fabrication of Microstructures by Optical Lithography for Electric Trapping of Polar Molecules — ●MARTIN IBRÜGGER, MARKUS KROTTENMÜLLER, ALEXANDER PREHN, ROSA GLÖCKNER, MARTIN ZEPPENFELD, and GERHARD REMPE — Max-Planck-Institut für Quantenoptik, Hans-Kopfermann-Str. 1, 85748

Polar molecules cooled to cold and ultracold temperatures offer a wide range of exciting applications ranging from quantum simulation to controlled chemistry. For such experiments, providing a suitable environment to confine the molecules is often essential. For this purpose, a unique design for an electric trap based on confining molecules between a pair of microstructured capacitor plates [1] has allowed us to achieve record-long trap lifetimes [2] and to cool the molecules' motional and rotational degrees of freedom [3,4].

To further improve the properties of our trap, we are currently investigating the in-house fabrication of the trap microstructures based on well-known optical lithography techniques combined with chemical wet etching. Here, we in particular aim for a good high voltage performance combined with minimal surface charges. We present details of our fabrication method as well as the results from high voltage tests.

[1] M. Zeppenfeld *et al.*, *Phys. Rev. A* **80**, 041401 (2009).

[2] B.G.U. Englert *et al.*, *Phys. Rev. Lett.* **107**, 263003 (2011).

[3] M. Zeppenfeld *et al.*, *Nature* **491**, 570-573 (2012).

[4] R. Glöckner *et al.*, *submitted* (2015).

MO 21.17 Thu 17:00 C/Foyer

Manipulating the motion of neutral polar molecules with microwave fields — ●SIMON MERZ¹, JACK B. GRANEK¹, NICOLAS VANHAECKE², GERARD MEIJER^{2,3}, and MELANIE SCHNELL¹ — ¹Max-Planck-Institut für Struktur und Dynamik der Materie am Center for Free-Electron Laser Science, D-22761 Hamburg — ²Fritz-Haber-Institut der Max-Planck-Gesellschaft, D-14195 Berlin — ³Institut for Molecules and Materials at the Radboud University Nijmegen, NL-6525 AJ Nijmegen

An important remaining challenge in the field of cold molecules is a widely applicable method to manipulate the motion of neutral polar molecules in high-field-seeking states. This is a crucial step towards control of cold molecules in their ground states and of large and more complex molecules. As an alternative to the already demonstrated but discontinued alternating gradient methods, we use the interaction of polar molecules with cavity-enhanced microwave fields. Cylindrical microwave resonators provide transverse-electric field modes that are ideally suited for deceleration experiments [1-3].

Here, we present the latest results of our microwave deceleration experiments [3], using pre-decelerated packets of ammonia molecules and show first steps towards motion control of a beam of cold 4-aminobenzonitrile molecules.

[1] H. Odashima *et al.*, *Phys. Rev. Lett.* **104**:253001 (2010).

[2] S. Merz, *et al.*, *Phys. Rev. A*. **85**:063411 (2012).

[3] S. Merz, *et al.*, *Mol. Phys.* **111**:1855-1864 (2013).

MO 21.18 Thu 17:00 C/Foyer

Dynamics of H₂⁺ in intense laser fields: Full-dimensional approximate quantum-mechanical description of dissociation and ionization — ●TOBIAS FIEDLSCHUSTER, JAN HANDT, FRANK

GROSSMANN, and RÜDIGER SCHMIDT — Technische Universität Dresden

So far, even for nature's simplest molecule H_2^+ , no exact quantum-mechanical description of the laser-induced dynamics (i. e., simultaneously including vibration, rotation, dissociation and ionization) has been achieved.

In this work, we present a full-dimensional approximate quantum-mechanical treatment. It is based on the extension of a recently developed ab-initio Born-Oppenheimer surface hopping approach (M. Fischer, J. Handt and R. Schmidt, Phys.Rev. A 90, 012525 (2014), *ibid* 012526, *ibid* 012527) to hopping between Floquet surfaces.

The obtained results for dissociation and ionization are in very good agreement with recent experimental data (J. McKenna et al., Phys. Rev. A 85, 023405 (2012)).

The extension of the method to many-electron molecules is discussed.

MO 21.19 Thu 17:00 C/Foyer

Simulating 3D flexible Rydberg aggregates with surface hopping — ●KARSTEN LEONHARDT, SEBASTIAN WÜSTER, and JAN MICHAEL ROST — Max Planck Institute for the Physics of Complex Systems

Flexible Rydberg aggregates [1] are assemblies of highly excited light atoms, which are set into directed motion by resonant dipole-dipole interaction [1-4]. They provide a clean platform to study phenomena such as entanglement transport [2,3] and coherent splitting of excitons [4]. Very useful for the simulation of these systems is the surface hopping algorithm (FSSH) [5]. Nevertheless, to study these aggregates in 3D [TALK: A 270], a modification of the FSSH algorithm is needed, which we present here together with recent results of flexible Rydberg aggregates.

References

- [1] C. Ates, A. Eisfeld, J. M. Rost, *New. J. Phys.* **10**, 045030 (2008).
- [2] S. Wüster, C. Ates, A. Eisfeld, J. M. Rost, *Phys. Rev. Lett.* **105**, 195392 (2010).
- [3] S. Möbius, S. Wüster, C. Ates, A. Eisfeld, J. M. Rost, *J. Phys. B.* **44**, 184011 (2011).
- [4] K. Leonhardt, S. Wüster, J. M. Rost, *Phys. Rev. Lett.* **113**, 223001 (2014).
- [4] J. C. Tully, *J. Chem. Phys.* **93**, 1061 (1990).

MO 21.20 Thu 17:00 C/Foyer

Novel setup for a laser-based terahertz-field-driven extreme ultraviolet streak camera allowing for time resolved measurements of the full angle and kinetic energy distribution of electrons — ●MARTIN RANKE, FAWAD KARIMI, MARKUS PFAU, THOMAS GEBERT, and ULRIKE FRÜHLING — Institut für Experimentalphysik, Luruper Chaussee 149, 22761 Hamburg, Deutschland

In this work, a novel setup of a terahertz (THz) -field-driven extreme ultraviolet (XUV) streak camera for studying femtosecond dynamics in atoms and molecules is presented. High-harmonic generated XUV-pulses are synchronized and superimposed with intense single-cycle

THz pulses in a gas target. The XUV pulses are used to excite and ionize atoms or molecules. The resulting electrons are accelerated by the electric THz field which directly relates the change of the momentum to the THz vector potential. The kinetic energies of the electrons are measured fully angle resolved by a new velocity map imaging (VMI) spectrometer. The intense THz pulses are generated with a tilted pulse front setup of near infrared laser pulses by means of optical rectification in a nonlinear crystal.

MO 21.21 Thu 17:00 C/Foyer

Optimized focusing injector for single-particle coherent diffractive x-ray imaging — ●NILS ROTH^{1,2}, DANIEL HORKE¹, and JOCHEN KÜPPER^{1,2,3} — ¹Center for Free-Electron Laser Science, DESY — ²Department of Physics, University of Hamburg — ³Center for Ultrafast Imaging, University of Hamburg

Single-particle coherent diffractive imaging requires reproducible particles to build up a 3D molecular image [1]. Current experiments are limited by the inefficient delivery of particles and correspondingly low hit-rates, i.e., poor usage of sample and x-ray photons. We are developing a controllable and efficient vaporization and aerodynamic lens [2] system to provide tightly focused beams of nanoparticles and biological systems, which will efficiently be guided to the interaction point. Here, we present detailed numerical simulations, as well as experimental characterization, of such an aerodynamic lens system. In the future this will be combined with optical manipulation and guiding [3]. The increased hit-rate achieved in such a setup will make "molecular-movie" experiments possible.

- [1]Barty et al, *Annu. Rev. Phys. Chem.* **64** 415-435
- [2]Lui et al, *Aerosol Sci. Technol.* **22** 293-313
- [3]Eckerskorn et al, *Opt. Exp.* **21** 30492-30499

MO 21.22 Thu 17:00 C/Foyer

Lamb-Dip rotational spectroscopy of OCS in the mm-wave region — ●OLIVER ZINGSHEIM¹, JAKOB MASSEN¹, SVEN THORWIRTH¹, FRANK LEWEN¹, MARIE-ALINE MARTIN-DRUMEL^{1,2}, and STEPHAN SCHLEMMER¹ — ¹I. Physikalisches Institut, Köln, Germany — ²Harvard-Smithsonian Center for Astrophysics, Cambridge, USA

Carbonyl sulfide (OCS) is a widespread and important molecule in the interstellar medium (ref [1] and references therein). Because of its astronomical relevance and also its importance as a calibration gas in the laboratory the pure rotational spectrum is comparably well studied in particular that of the parent isotopic species (see, for example, ref [2]). Here, we report on high precision Lamb-Dip measurements of rare isotopic species in the frequency range from 75 to 370 GHz. The measurements were performed in a 5m absorption cell with a roof-top mirror to allow for double pass of the mm wave radiation. Transitions of singly substituted isotopologues were measured (¹³C, ¹⁷O, ¹⁸O, ³³S, ³⁴S) resulting in new significantly improved sets of molecular parameters. Further Lamb-Dip measurements of transient molecules will be performed in the near future.

- [1] A. Belloche, H. S. P. Müller, K. M. Menten, P. Schilke, C. Comito, *Astron. & Astrophys.* **559**, A47 (2013).
- [2] G.Yu. Golubiatnikov, A. V. Lapinov, A. Guarnieri, R. Knöchel, *J. Mol. Spectrosc.* **234** (2005) 190-194.

MO 22: Femtosecond Spectroscopy 3

Time: Friday 11:00–13:00

Location: PH/HS1

MO 22.1 Fri 11:00 PH/HS1

Effects of Conjugation on Molecular Dynamics — ●FEDERICO KOCH¹, ANDRÉ ZITZLER-KUNKEL², CRISTINA CONSANI¹, FRANK WÜRTHNER², and TOBIAS BRIXNER¹ — ¹Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg — ²Institut für Organische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

Interactions of chromophores and formation of excitons play a fundamental role in understanding the dynamics of molecules ranging from small molecular systems up to complex systems such as polymers and aggregates. To better understand these interactions a series of merocyanine dyes directly linked via a bridge was synthesized. This molecular series allows the comparison between interactions through space and interaction mediated by the bridge.

The differences in the absorption maxima and band splitting can in

principle be explained by a vibrational progression or a weak excitonic coupling. To investigate this we use transient absorption and compare the relaxation dynamics after excitation. Furthermore, we aim to directly visualize chromophore interaction by using polarization-dependent measurements and coherent 2D spectroscopy.

MO 22.2 Fri 11:15 PH/HS1

Phase-modulated fs pump-probe spectroscopy of RbHe exciplexes — ●LUKAS BRUDER, MARCEL BINZ, AARON LAFORGE, MARCEL MUDRICH, and FRANK STIENKEMEIER — Physikalisches Institut, Universität Freiburg, 79104 Freiburg

Due to the low target densities in molecular and doped He droplet beam experiments, coherent fs spectroscopy in such setups has remained a challenging task. In this context we are investigating a phase-modulation fs pump-probe technique established by Marcus et

al. [1]. The combination of continuous acousto-optical phase modulation with lock-in detection greatly improves the signal-to-noise ratio in this scheme. We have applied this method to our He droplet beam apparatus and acquired mass-resolved photo ionization spectra of RbHe exciplexes. This data reveals much higher resolution than was previously achieved with conventional pump-probe setups. Furthermore, one gains new insight into the energy structure of the exciplex.

[1] P. F. Tekavec, T. R. Dyke, and A. H. Marcus, *J. Chem. Phys.* 125, 194303 (2006).

MO 22.3 Fri 11:30 PH/HS1

Comparative quantum dynamical studies of two diphenylmethyl halide species in a quasi-diabatic picture states including three-state conical intersections — ●MATTHIAS K. ROOS, SEBASTIAN THALLMAIR, and REGINA DE VIVIE-RIEDLE — Department Chemie, Ludwig-Maximilians-Universität München

Carbocations and -radicals are key intermediates of many reactions both in organic synthesis and biochemistry. Such reactive species can be generated by UV laser irradiation of diphenylmethyl halides. This so triggered sub-picosecond ultrafast dissociation occurs via a local π - π^* excitation and finally the carbon-halide σ -bond cleavage is either homolytic or heterolytic. The halide, i.e. chlorine or bromine, acts as leaving group. We use both quantum chemical and quantum dynamical methods to model the bond cleavage and evaluate the branching ratio between the two product pathways. Based on a reduced coordinate space that explicitly includes geometry relaxation for the carbon skeleton the kinetic Hamiltonian is expressed via the Wilson G-Matrix approach. Potential energy surfaces are calculated on the ONIOM(CASSCF(12,10)/B3LPYP) level of theory showing consecutive conical intersections near the Franck-Condon region. Especially three-state conical intersections play the key role for the product splitting. Using *ab initio* properties the adiabatic potentials are transformed to a quasi-diabatic picture, therefore the off-diagonal potential terms are accounting for the non-adiabatic behaviour. The dynamics for both leaving groups is discussed and compared with experimental results.

MO 22.4 Fri 11:45 PH/HS1

Towards multi-dimensional Raman spectroscopy of excited electronic states in the time domain — ●TORSTEN WENDE, CHRISTOPH SCHNEIDERMAN, MATZ LIEBEL, and PHILIPP KUKURA — Physical & Theoretical Chemistry Laboratory, South Parks Road, Oxford OX1 3QZ

Many biological and chemical processes rely on an efficient transfer of photon energy into specific atomic motion. Following the nuclear motion directly after photoexcitation provides valuable structural information to elucidate the mechanism that governs the energy flow throughout a molecule. We have developed a time-domain approach for measuring time-resolved excited-state Raman spectra by means of population-controlled impulsive vibrational spectroscopy. Using an ultrashort actinic (<15 fs) and impulsive (<10 fs) pump pulse in combination with a narrowband dump control pulse allows us to experimentally isolate excited-state vibrational coherence and follow its temporal evolution. Here, we study the fast internal conversion (<100 fs) from the S2 into the S1 electronic state in diphenyl-octatetraene. The time-resolved Raman spectra reveal that vibrational coherence is efficiently transferred from S2 into S1. We observe large amplitudes in the 850, 1300 and 1550 cm^{-1} modes which decay according to the S2 lifetime, while the remaining modes decay primarily with the lifetime of S1. Extraction of a 2D correlation map exhibits signatures of vibrational coupling indicated by multiple cross-peaks between low-frequency modes and selected high-frequency modes.

MO 22.5 Fri 12:00 PH/HS1

Surface-Enhanced, 2D Attenuated Total Reflectance Infrared Spectroscopy At Solid-Liquid Interfaces — ●JAN PHILIP KRAACK, DAVIDE LOTTI, and PETER HAMM — Department of Chemistry, University of Zürich, Winterthurerstrasse 190, CH-8057

Femtosecond dynamics of molecules at solid-liquid and solid-gas interfaces have recently gained considerable attention in nonlinear spectroscopy. We present recent advances towards establishing a new experimental method which is capable for resolving coherent, ultrafast two-dimensional (2D) infrared (IR) spectra of molecules adsorbed on metallic thin films. (1) The method is based on measuring Attenuated Total Reflectance (ATR) signals at solid-liquid interfaces using metals for immobilization of the samples. We present details of the femtosecond 2D ATR IR technique together with benchmarking results

from small molecules as well as organic monolayers. (2) The nonlinear signals are investigated in terms of surface-enhancement effects (3) and environmental interactions. It is demonstrated that 2D ATR IR spectroscopy allows a surface-sensitive characterization of vibrational lifetimes, dephasing, spectral diffusion and sample inhomogeneity on the femtosecond timescale.

(1) Kraack, J. P.; Lotti, D.; Hamm, P., *JPC Lett.* 2014, 18, 2325.

(2) Kraack, J. P.; Lotti, D.; Hamm, P., in preparation.

(3) Donaldson, P. M.; Hamm, P., *Angew. Chemie* 2013, 125, 662.

MO 22.6 Fri 12:15 PH/HS1

Ultrafast Dissociation Dynamics of Superexcited Nitrogen — ●JOHAN HUMMERT¹, MARTIN ECKSTEIN¹, DANIEL STRASSER², MARC J. J. VRAKING¹, and OLEG KORNILOV¹ — ¹Max Born Institut, Berlin, Germany — ²Institute of Chemistry, The Hebrew University of Jerusalem, Israel

Understanding relaxation pathways of neutral superexcited states in elementary molecules is important to model the chemistry of environments exposed to XUV and other ionizing radiation. Such species occur in terrestrial and extraterrestrial atmospheres and in man-made environments. Additionally the coupling of electronic and nuclear degrees of freedom in superexcited states is particularly interesting since the Born-Oppenheimer approximation is often strongly violated.

In this experimental work we investigate dissociation dynamics of superexcited states of molecular nitrogen excited by pulsed XUV light. We employ a high harmonic generation source in combination with a time-compensating XUV monochromator to select the 15th harmonic of a 790 nm IR laser pulse at 23.6 eV, which is just below the threshold for dissociative ionization of N_2 (24.25 eV). A second laser pulse at the wavelength of 790 nm probes the highly excited molecules or fragments after a time-delay ionizing them to produce the detected N^+ ions.

The recorded transient signals demonstrate both a very quickly decaying component (about 40 fs) as well as a long-lived contribution. Preliminary assignments suggest competition between predissociation from Rydberg-type states converging to the ionic $C^2\Sigma_u^+$ state and autoionization leading to bound ions.

MO 22.7 Fri 12:30 PH/HS1

Reaction-sensitive tracking of ultrafast chemical reaction dynamics with pump-dump spectroscopy — ●ALEX S. DUARTE, GIOVANNI BASSOLINO, CHRISTOPH SCHNEIDERMAN, JONGMIN LIM, TORSTEN WENDE, and PHILIPP KUKURA — Physical & Theoretical Chemistry Laboratory, South Parks Road, Oxford OX1 3QZ

The retinal protonated Schiff base (RPSB) chromophore has become a paradigmatic photochemical system due to its widespread involvement in biological photoreceptors. One of the most puzzling and most studied aspects of RPSB photochemistry is the dramatic increase in reaction speed and yield in the protein over the solution environment, which has been attributed to a specific interaction of the chromophore with an evolution-optimised protein pocket.

Here, we combine excitation of RPSB in solution with a resonant 20 fs optical pulse followed by a 10 fs dump pulse that only serves to control the excited state population. By monitoring the photoproduct formation through changes in the transient absorption spectrum of RPSB at long time delays (60 ps) as a function of pump-dump-delay we reveal the earliest excited state relaxation dynamics for both 11-cis and all-trans RPSB in solution. Remarkably, the experiment reveals an ultrafast (<100 fs) photoisomerization channel for 11-cis RPSB in contrast to all-trans RPSB, closely resembling the dynamic behaviour of 11-cis RPSB in rhodopsin during the first step of vision.

MO 22.8 Fri 12:45 PH/HS1

Real-time tracking of structural rearrangements in wt-GFP after photoexcitation — ●CHRISTOPH SCHNEIDERMAN, TORSTEN WENDE, GIOVANNI BASSOLINO, MATZ LIEBEL, and PHILIPP KUKURA — Physical & Theoretical Chemistry Laboratory, South Parks Road, Oxford OX1 3QZ

A vast number of biological and chemical processes rely on the efficient conversion of photon energy into atomic motion. In order to understand the factors determining the energy flow after photoexcitation, it is necessary to track the atomic motion in real-time directly after the absorption of a photon has occurred. Here, we present a time-domain approach capable of resolving the temporal evolution of excited state nuclear degrees of freedom with broadband impulsive vibrational spectroscopy. An actinic pump pulse (15 fs) excites the system followed, after a variable time-delay, by an impulsive Raman pulse (10 fs), which generates vibrational coherences in all excited molecules. These coher-

ences are subsequently recorded by a probe pulse for varying actinic-impulsive pump delay. We use this approach to investigate the excited state proton transfer in wild-type green fluorescent protein and reveal signatures of vibrational coupling between FC and excited state

nuclear degrees of freedom akin to multi-dimensional infrared spectroscopy. The observed cross-peaks throughout the fingerprint regime reveal the atomic motions occurring during proton-transfer after photoexcitation.

MO 23: Progress on Various Topics in Molecular Physics

Time: Friday 11:00–12:45

Location: PH/SR106

MO 23.1 Fri 11:00 PH/SR106

Torsion and Bending Motion of ^{13}C Substituted Dimethyl Ether — ●PIA KUTZER¹, OLIVIER PIRALI², PASCALE ROY², and THOMAS GIESEN¹ — ¹Universität Kassel, Institut für Physik, Heinrich-Plett Str. 40, D-34132 — ²Société civile Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin - BP 48, F-91192 Gif Sur Yvette Cedex

Dimethyl ether (DME) shows large amplitude internal motion. The internal torsion of both methyl groups exhibits strong coupling effects of the rotors and with the C-O-C in plane bending mode.

The molecule is well-studied by means of high resolution spectroscopy, although there are still some important open questions left, especially in case of the ^{13}C substituted species. Calculated band centre frequencies of the torsional motion obtained from high level *ab initio* calculations still deviate from experimental values, and comparison to ^{13}C substituted species was so far restricted to few measurements of pure rotational transitions.

Recently, we recorded first high resolution broadband spectra of singly and doubly ^{13}C substituted DME using a FT-IR spectrometer at SOLEIL synchrotron laboratories. We also recorded spectra of these species at Kassel at a lower resolution.

Here we present our ongoing analysis of the C-O-C bending mode of the three isotopologues and preliminary results for the first torsionally excited states.

Our measurements and analyses will help to foster quantum chemical modelling of large amplitude motion.

MO 23.2 Fri 11:15 PH/SR106

Investigation of ETFE Plastic Foils Using Raman Spectroscopy and Chemometric Analysis — ●ALEXANDRU POPA, RASHA HASSANEIN, and ARNULF MATERNY — Jacobs University, Campus Ring 1, 28759 Bremen, Germany

Ethylene-tetra-fluoro-ethylene (ETFE) is a fluorine-based plastic, which presents excellent thermal and mechanical properties such as durability, flexibility, as well as light-weight, low frictional coefficient, long-term stability against solar degradation, and transmissivity of all visible wavelengths. Due to these outstanding characteristics, ETFE foils have become more and more popular in building applications, as roofing. Within the current contribution, ETFE samples produced by two manufacturers and with coatings applied by different companies have been investigated using confocal micro Raman spectroscopy with 514.5nm excitation. The confocal setup allowed for high depth resolution required to access the interface between coating and ETFE foil. The aim of the study was the comparison of print quality from two manufacturers for different ink types, as well as the correlation of print quality to the adhesion of the ink onto the surface of the foil. Samples were obtained and Raman spectroscopically investigated at different time-steps: after the coating took place and at different times while they were exposed to an accelerated weathering system with UV radiation, heat, and humidity. Changes seen in the Raman spectra will be discussed.

MO 23.3 Fri 11:30 PH/SR106

Tuning the non-radiative lifetime of molecular aggregates via the dipole-dipole interaction — ●ALAN CELESTINO and ALEXANDER EISFELD — MPIPKS, Dresden, Germany

Non-radiative transitions lead in many molecules to a relaxation from the electronic excited to the ground state on a time scale faster than that of spontaneous emission. Therefore the excitonic lifetime in those molecules is limited by their non-radiative transition channels. Depending on the application in mind one would like to tune these lifetimes (making them longer or shorter). Here we show that aggregation of such molecules strongly influences the non-radiative lifetime. By varying the dipole-dipole interaction between the molecules one can either enhance the the non-radiative lifetime or even totally suppress

it. We study in detail a molecular dimer. The monomer is modeled as a two electronic level system coupled to a single nuclear coordinate (relevant nuclear coordinate). The remaining nuclear coordinates are taken into account as a Markovian bath coupled to the relevant nuclear coordinate. The two electronic potential surfaces are coupled via a non-radiative well-localized exciton-decay channel. The dimer is composed by two dipole-dipole-interacting monomers. The dipole-dipole interaction leads to completely new dynamics and allows one to tune the excitonic lifetime.

MO 23.4 Fri 11:45 PH/SR106

Matrix Completion: Enhancing the Measurement Efficiency in 2D Spectroscopy — ●MATTHIAS KOST — Department of Theoretical Physics, Ulm University, Germany

2D spectroscopy is an indispensable tool in various modern sciences like physics, biology, chemistry and medicine. In particular, it resolves useful information about the inner electronic and spatial structure of molecules in a sample. However, the gain of high resolution requires a large number of measurements, which is one of the central problems concerning measurement efficiency.

Matrix completion is a mathematical procedure, providing the ability to recover certain matrices from just a few of its entries. This talk demonstrates, how the application of such algorithms in the context of 2D spectroscopy leads to significantly less measurement effort. This enhancement may be a crucial step towards the feasibility of more complex 2D spectroscopy methods.

MO 23.5 Fri 12:00 PH/SR106

The Bending Vibration of the C_3 -Molecule and its Isotopologues in the Terahertz Region — ●THOMAS BÜCHLING, ALEXANDER BREIER, GUIDO FUCHS, and THOMAS GIESEN — Universität Kassel, Institut für Physik, Heinrich-Plett Str. 40, 34132 Kassel

Short carbon chains are fundamental for the chemistry of stellar and interstellar ambiances: They are omnipresent throughout the interstellar medium, they likely participate in the formation of long carbon chains and they are products in photo-fragmentation processes of larger species.

Triatomic carbon C_3 exhibits a mid-infrared ν_3 antisymmetric stretching mode and a ν_2 bending vibration at 1.9 THz. The detection of ν_2 is experimentally challenging as radiation sources in the terahertz frequency region were missing for a long time as they are in the transition area between optical and microwave techniques.

In our experiment carbon is vaporized by laser-ablation and diluted in a supersonic jet of helium. Through absorption spectroscopy the molecular constants of the main isotopologue $^{12}\text{C}^{12}\text{C}^{12}\text{C}$ and of singly ^{13}C substituted species are derived.

These laboratory measurements are taken as a basis for further astrophysical observations of different C_3 -isotopologues. This will lead to a better understanding of the chemistry of the stellar and interstellar medium.

MO 23.6 Fri 12:15 PH/SR106

Diffraction imaging of dissociating molecules using X-ray free-electron lasers — ●FENGLIN WANG^{1,2}, STEPHAN STERN¹, HENRY N. CHAPMAN^{1,3,4}, and JOCHEN KÜPPER^{1,3,4} — ¹Center for Free-Electron Laser Science (CFEL), DESY, 22607 Hamburg, Germany — ²PULSE Institute, Stanford University, Stanford, California 94305, USA — ³Department of Physics, University of Hamburg, Luruper Chaussee 149, 22671 Hamburg, Germany — ⁴Center for Ultrafast Imaging (CUI), University of Hamburg, 22607 Hamburg, Germany

Free-electron lasers (FELs) can provide very intense, ultrashort pulses of coherent X-rays. This allows for diffractive techniques to see single molecules at spatially and temporally atomic resolution (pm and fs). We use ensembles of laser-aligned isolated molecules to demonstrate these imaging techniques with FELs and to record “molecular movies” of structural dynamics in a bottom-up approach. Here, we present a

holographic idea that allows to disentangle the multiple simultaneously pathways occurring in the photodissociation of complex molecules. In this *fragmentation holography* the incoherent contributions from different pathways are directly separable in the Fourier transform of the diffraction patterns. This will enable us to gain access to structural information of fragmenting molecules as a function of pathways and time.

MO 23.7 Fri 12:30 PH/SR106

Relativistic Density Functional Calculations of Chemical Shifts of Manganese K X Rays — BURKHARD FRICKE¹, ●KHALID RASHID², and DETLEV GOTTA³ — ¹Institut für Physik, Universität Kassel, Germany — ²National University of Science and Technology, Islamabad, Pakistan — ³Institut für Kernphysik, Forschungszentrum Jülich, Germany

The complexity of the origin of the K energy shifts arising from the

electronic structure of 3d electrons in the Liegand field of the compound makes the interpretation a formidable problem. Here a theoretical attempt is made to understand the K energy shifts of Mn atom coming from different chemical environment measured by D. Gotta et. al. Relativistic density functional theory calculations are made with the CLUSTER code developed at Kassel University. The chemical environment of the Mn compound is simulated by a model cluster of six closest neighbour atoms placed on a grid. Vectors of the neighbour atoms are extracted from the available data of electronic structure of Mn compounds. The $K\alpha_1$ and $K\alpha_2$ line energies are determined by calculating the total energies of the complex of manganese and its six neighbour atoms for 1s, 2p_{1/2}, and 2p_{3/2} hole states and building their differences. Calculated K shifts for $K\alpha_2$ are of the same order of magnitude as the measured shifts except for the MnF₃ case. For $K\alpha_1$ shifts however the spread between theory and experiment is relatively larger.