

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: BEBEL HS213 and SR144; Posters: Spree-Palais)

Invited and Topical Talks

MO 1.1	Mon	10:30–11:00	BEBEL HS213	Strongly driven quantum pendulum of a polar molecule — •SEBASTIAN TRIPPEL, TERENCE G. MULLINS, NELE L.M. MÜLLER, JENS S. KIENITZ, ROSARIO GONZÁLEZ-FÉREZ, JOCHEN KÜPPER
MO 3.1	Mon	14:00–14:30	BEBEL HS213	Imaging the Absolute Configuration of a Chiral Epoxide in the Gas Phase — •HOLGER KRECKEL, PHILIPP HERWIG, KERSTIN ZAWATZKY, MANFRED GRIESER, ODED HEBER, BRANDON JORDON-THADEN, CLAUDE KRANTZ, OLDŘICH NOVOTNÝ, ROLAND REPNOW, VOLKER SCHURIG, DIRK SCHWALM, ZEEV VAGER, ANDREAS WOLF, OLIVER TRAPP
MO 3.4	Mon	15:00–15:30	BEBEL HS213	Circular Dichroism in Mass Spectrometry: Laser Pulse Induced Electron Wavepacket Dynamics — •DOMINIK KRÖNER
MO 4.1	Mon	14:00–14:30	BEBEL SR144	Ultracold Rydberg plasma formation in intense laser-cluster interactions: resolving the mystery of highly charged ions — •THOMAS FENNEL
MO 6.1	Tue	10:30–11:00	BEBEL HS213	Time-resolved absorption studies of photoinitiator molecules in solution — •ANDREAS-NEIL UNTERREINER, HANNA A. ERNST, THOMAS J. A. WOLF, DOMINIK VOLL, ELENA FRICK, CHRISTOPHER BARNER-KOWOLLIK
MO 8.1	Tue	14:00–14:30	BEBEL HS213	Selected Personal Highlights of Electron Collision Work — •MICHAEL ALLAN
MO 12.1	Wed	14:00–14:30	BEBEL SR144	Ultrafast X-ray Auger Probing of photoexcited molecular dynamics — B. K. MCFARLAND, J. FARRELL, S. MIYABE, F. TARANTELLI, A. AGUILAR, N. BERRAH, C. BOSTEDT, J. D. BOZEK, P. H. BUCKSBAUM, J. C. CASTAGNA, R. N. COFFEE, J. P. CRYAN, L. FANG, R. FEIFEL, K. J. GAFFNEY, J. M. GLOWNIA, T. J. MARTINEZ, M. MUCKE, B. MURPHY, A. NATAN, T. OSIPOV, V. S. PETROVIC, S. SCHORB, TH. SCHULTZ, L. S. SPECTOR, M. SWIGGERS, I. TENNEY, S. WANG, J. L. WHITE, W. WHITE, •M. GUEHR
MO 17.1	Thu	14:00–14:30	BEBEL HS213	Non-adiabatic relaxation dynamics in perylene bisimide dimers excited by femtosecond laser pulses — •VOLKER ENGEL, BERND ENGELS, MIRJAM FALGE, MARTIN KESS, STEFAN LOCHBRUNNER, ALEXANDER SCHUBERT, VOLKER SETTELS, WALTER STRUNZ, FRANK WÜRTHNER

Invited talks of the joint symposium SYCS

See SYCS for the full program of the symposium.

SYCS 1.1	Mon	10:30–11:00	Audimax	Electron dynamics in chiral systems: From structure determination to violation of fundamental symmetries — •ROBERT BERGER
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SYCS 1.2	Mon	11:00–11:30	Audimax	Electron Scattering in Chiral Photoionization: probing fundamental electron-molecule interactions to chiral molecular recognition — ●IVAN POWIS
SYCS 1.3	Mon	11:30–12:00	Audimax	Enantiomer Identification of Chiral Molecules in Mixtures using Microwave Three-Wave Mixing — ●MELANIE SCHNELL
SYCS 1.4	Mon	12:00–12:30	Audimax	Mass-selective circular dichroism spectroscopy of chiral molecules — ●ULRICH BOESL

Invited talks of the joint symposium SYAD

See SYAD for the full program of the symposium.

SYAD 1.1	Tue	10:30–11:00	Audimax	Rotationally resolved fluorescence spectroscopy - from neurotransmitter to conical intersection — ●CHRISTIAN BRAND
SYAD 1.2	Tue	11:00–11:30	Audimax	Quantum simulations with ultracold atoms: Beyond standard optical lattices — ●PHILIPP HAUKE
SYAD 1.3	Tue	11:30–12:00	Audimax	Degenerate quantum gases of alkaline-earth atoms — ●SIMON STELLMER
SYAD 1.4	Tue	12:00–12:30	Audimax	One step beyond entanglement: general quantum correlations and their role in quantum information theory — ●ALEXANDER STRELTSOV

Prize talks of the joint symposium SYAW

See SYAW for the full program of the symposium.

SYAW 1.1	Wed	14:00–14:30	Kinosaal	Semicrystalline polymers - pathway of crystallization and deformation properties — ●GERT STROBL
SYAW 1.2	Wed	14:30–15:00	Kinosaal	A measurement of the evolution of Interatomic Coulombic Decay in the time domain — ●TILL JAHNKE
SYAW 1.3	Wed	15:00–15:30	Kinosaal	A one-dimensional liquid of fermions with tunable spin — ●MASSIMO INGUSCIO
SYAW 1.4	Wed	15:30–16:00	Kinosaal	Non-equilibrium: from heat transport to turbulence (to life). — ●DAVID RUELLE
SYAW 2.1	Wed	16:30–17:00	Kinosaal	Investigation of charge transfer efficiency of CCD image sensors for the scientific small satellite mission “AsteroidFinder” — ●ANDREJ KRIMLOWSKI
SYAW 2.2	Wed	17:00–17:30	Kinosaal	Metrology of atomic hydrogen: from the Rydberg constant to the size of the proton — ●FRANÇOIS BIRABEN

Invited talks of the joint symposium SYSE

See SYSE for the full program of the symposium.

SYSE 1.1	Wed	14:00–14:30	Audimax	Addressing open questions of stellar evolution with laboratory experiments — ●ALMUDENA ARCONES
SYSE 1.2	Wed	14:30–15:00	Audimax	Methods and problems of the modern theory of stellar evolution — ●ACHIM WEISS
SYSE 1.3	Wed	15:00–15:30	Audimax	Photoabsorption and opacity in the X-ray region: The role of highly charged ions — ●JOSÉ R. CRESPO LÓPEZ-URRUTIA
SYSE 1.4	Wed	15:30–16:00	Audimax	Neutron-rich matter: From cold atoms to neutron stars — ●ACHIM SCHWENK

Invited talks of the joint symposium SYRE

See SYRE for the full program of the symposium.

SYRE 1.1	Wed	16:30–17:00	Audimax	Rare and large events: examples from the natural sciences and economics — ●THOMAS GUHR
SYRE 1.2	Wed	17:00–17:30	Audimax	The roles of energy-level and electronic-coupling fluctuations in the control of biomolecular and small-molecule charge transfer reactions — ●SPIROS SKOURTIS

SYRE 1.3	Wed	17:30–18:00	Audimax	What do we know about extreme solar events? — ●ILYA USOSKIN
SYRE 1.4	Wed	18:00–18:30	Audimax	The climate impact of very large volcanic eruptions: An Earth system model approach — ●CLAUDIA TIMMRECK

Invited talks of the joint symposium SYET

See SYET for the full program of the symposium.

SYET 1.1	Thu	10:30–11:00	SPA Kapelle	On the role of charge transfer excitations in mediating triplet diffusion, singlet fission and dissociation in organics — ●DAVID BELJONNE
SYET 1.2	Thu	11:00–11:30	SPA Kapelle	Disorder engineered long-range exciton migration in J-aggregates - observation of fluorescence from low-laying individual Lévy states — ●IVAN SCHEBLYKIN, ABOMA MERDASA, ÁNGEL JIMÉNEZ, THEO KAISER, FRANK WÜRTHNER
SYET 1.3	Thu	11:30–12:00	SPA Kapelle	Quantum dynamics of molecular and atomic aggregates — ●ALEXANDER EISFELD
SYET 1.4	Thu	12:00–12:30	SPA Kapelle	Energy transport in ultracold Rydberg aggregates — ●MATTHIAS WEIDEMÜLLER

Invited talks of the joint symposium SYPS

See SYPS for the full program of the symposium.

SYPS 1.1	Thu	14:10–14:40	Audimax	Oxygen and imaging, a perfect match — ●DAVID PARKER
SYPS 1.2	Thu	14:40–15:10	Audimax	Attosecond imaging — ●MARC VRAKING
SYPS 1.4	Thu	15:25–15:55	Audimax	Applications of the fast imaging Pixel Imaging Mass Spectrometry camera — ●MARK BROUARD
SYPS 2.1	Thu	16:30–17:00	Audimax	Unraveling the dynamics of state- and conformer selected molecules fixed in space with the VMI — ●JOCHEN KÜPPER
SYPS 2.3	Thu	17:15–17:45	Audimax	Velocity map imaging: from molecules to clusters, nanoparticles and aerosols — ●MICHAL FARNIK, VIKTORIYA POTERYA, JOZEF LENGYEL, ANDRIY PYSANENKO, PAVLA SVRCKOVA, JAROSLAV KOCISEK
SYPS 2.5	Thu	18:00–18:30	Audimax	Velocity map imaging studies of quantum state resolved scattering at gas-solid and gas-SAMs surfaces — ●DAVID J. NESBITT, MONIKA GRUETTER, J. ROBERT ROSCIOLI, CARL HOFFMAN, DANIEL J. NELSON

Invited talks of the joint symposium SYQS

See SYQS for the full program of the symposium.

SYQS 1.1	Fri	10:30–11:15	Audimax	Tutorial Complex Systems: From Classical to Quantum, from Single to Many Particle Problems — ●KLAUS RICHTER
SYQS 1.2	Fri	11:30–12:00	Audimax	Multiphoton random walks: Experimental Boson Sampling on a photonic chip — ●IAN WALMSLEY, JUSTIN SPRING, BEN METCALF, PETER HUMPHREYS, STEVE KOLTHAMMER, XIANMIN JIN, ANIMESH DATTA, JAMES GATES, PETER SMITH
SYQS 2.1	Fri	14:00–14:30	Audimax	Charge transfer and quantum coherence in solar cells and artificial light harvesting systems — ●CHRISTOPH LIENAU
SYQS 2.6	Fri	15:30–16:00	Audimax	Feedback control: from Maxwell's demon to quantum phase transitions — ●TOBIAS BRANDES
SYQS 3.4	Fri	17:15–17:45	Audimax	Multi-photon dynamics in complex integrated structures — ●FABIO SCIARRINO
SYQS 3.5	Fri	17:45–18:15	Audimax	Complexity and many-boson coherence — ●MALTE TICHY

Sessions

MO 1.1–1.7	Mon	10:30–12:30	BEBEL HS213	Cold Molecules 1
MO 2.1–2.8	Mon	10:30–12:30	BEBEL SR144	Clusters
MO 3.1–3.6	Mon	14:00–16:00	BEBEL HS213	Chiral Systems (SYCS 2)

MO 4.1–4.7	Mon	14:00–16:00	BEBEL SR144	Theory 1: Molecular Dynamics
MO 5.1–5.28	Mon	16:30–18:30	Spree-Palais	Posters 1: Electronic Spectroscopy, Photochemistry, Femtosecond Spectroscopy
MO 6.1–6.6	Tue	10:30–12:15	BEBEL HS213	Femtosecond Spectroscopy 1
MO 7.1–7.8	Tue	10:30–12:30	BEBEL SR144	Experimental Techniques 1
MO 8.1–8.7	Tue	14:00–16:00	BEBEL HS213	Electronic Spectroscopy 1
MO 9.1–9.8	Tue	14:00–16:00	BEBEL SR144	Theory 2: Molecular Dynamics & Quantum Chemistry
MO 10.1–10.28	Tue	16:30–18:30	Spree-Palais	Posters 2: Biomolecules, Energy Transfer, Clusters, Quantum Chemistry, Molecular Dynamics and Chirality
MO 11.1–11.7	Wed	14:00–15:45	BEBEL HS213	Biomolecules 1
MO 12.1–12.5	Wed	14:00–15:30	BEBEL SR144	Experimental Techniques 2
MO 13.1–13.40	Wed	16:30–18:30	Spree-Palais	Posters 3: Cold Molecules, Helium Nano Droplets, and Experimental Techniques
MO 14.1–14.8	Thu	10:30–12:30	BEBEL HS213	Cold Molecules 2
MO 15.1–15.7	Thu	10:30–12:15	BEBEL SR144	Experimental Techniques 3
MO 16.1–16.7	Thu	10:30–12:30	BEBEL E44/46	Atomic clusters (with A)
MO 17.1–17.5	Thu	14:00–15:30	BEBEL HS213	Excitons and Excitation Transfer (SYET 2)
MO 18.1–18.7	Thu	14:00–15:45	BEBEL SR144	Theory 3: Quantum Chemistry
MO 19.1–19.7	Thu	16:30–18:15	BEBEL HS213	Femtosecond Spectroscopy 2
MO 20.1–20.8	Thu	16:30–18:30	BEBEL SR144	Electronic Spectroscopy 2
MO 21.1–21.8	Fri	10:30–12:30	BEBEL HS213	Photochemistry
MO 22.1–22.6	Fri	10:30–12:00	BEBEL SR144	Cold Molecules 3
MO 23.1–23.7	Fri	14:00–15:45	BEBEL HS213	Femtosecond Spectroscopy 3
MO 24.1–24.6	Fri	14:00–15:30	BEBEL SR144	Biomolecules 2

Annual General Meeting of the Molecular Physics Division

Dienstag 12:30–13:00 BEBEL HS213

- Bericht
- Verschiedenes

MO 1: Cold Molecules 1

Time: Monday 10:30–12:30

Location: BEBEL HS213

Invited Talk

MO 1.1 Mon 10:30 BEBEL HS213

Strongly driven quantum pendulum of a polar molecule

— ●SEBASTIAN TRIPPEL¹, TERENCE G. MULLINS¹, NELE L.M. MÜLLER¹, JENS S. KIENITZ^{1,2}, ROSARIO GONZÁLEZ-FÉREZ⁴, 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 — ⁴Instituto Carlos I de Física Teórica y Computacional and Departamento de Física Atómica, Molecular y Nuclear, Universidad de Granada, Spain

The behavior of molecules subject to strong laser fields has been a rapidly growing topic in molecular physics and chemistry during the last years. The anisotropic interaction between an isolated molecule and a nonresonant, linearly polarized laser field creates pendular states, i. e., directional superpositions of field-free rotational states [1]. We disentangled the rotational and pendular state wavepacket dynamics of quantum state selected carbonyl sulfide (OCS) molecules. A strong oscillation on the degree of alignment is observed that resembles the motion of a classical pendulum. Features in the transition from impulsive, non-adiabatic to adiabatic alignment and orientation were disentangled, with implications on the switching behavior of fast molecular switches in non dissipative media. In addition, we demonstrated how the combination of quantum state selection and rotational coherence spectroscopy allows for a complete measurement of magnitude and polarization of angular momenta of molecules in field-free space.

[1] B. Friedrich and D. Herschbach, *Phys. Rev. Lett.* **74**, 4623 (1995)

MO 1.2 Mon 11:00 BEBEL HS213

Superfluid Helium Solvation Effects on Hydrogen Bonded Molecules

— ●LUKASZ WALEWSKI, HARALD FORBERT, and DOMINIK MARX — Ruhr-Universität Bochum, Bochum, Deutschland

Atomic nuclei become delocalized at low temperatures as a result of quantum effects. For non-interacting atoms the magnitude of this effect increases upon lowering the temperature according to the thermal de Broglie wavelength of free particles. However, strong interactions due to chemical bonding that set in for atoms bound in molecules, counteract this tendency resulting in the, so called, “interaction induced localization”. This effect turns out to be extremely pronounced at ultra-low temperatures of about 1 K, characteristic to superfluid helium nanodroplets. The most affected are protons shared in hydrogen bonds [1], which are confined to a spatial region that corresponds to about 0.1% of the volume occupied by a non-interacting proton at the same temperature. Moreover, applying our recently developed hybrid *ab initio* MD / bosonic MC path integral method [2] to an HCl/water cluster, HCl(H₂O)₄, we find that helium solvation has a significant additional localizing effect. In particular, the solvent-induced excess localization is the stronger the lesser the given nucleus is already localized in the gas phase reference situation [3].

[1] Walewski, L.; Forbert, H.; Marx, D. *Mol. Phys.*, **2013**, *111*, 2555.

[2] Walewski, L.; Forbert, H.; Marx, D. *Comp. Phys. Comm.* (accepted).

[3] Walewski, L.; Forbert, H.; Marx, D. *J. Chem. Phys.* (submitted).

MO 1.3 Mon 11:15 BEBEL HS213

Electron gun for diffraction experiments of controlled gas-phase molecules

— ●NELE L. M. MÜLLER¹, SEBASTIAN TRIPPEL¹, TERENCE G. MULLINS¹, JENS S. KIENITZ^{1,2}, KAROL DŁUGOLECKI¹, 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. Time-resolved structural information can be gained through various techniques, for example, by electron diffraction experiments. This contribution presents our newly set-up electron gun that will be combined with an existing controlled-molecules apparatus. The gas-phase molecules are prepared in cold, supersonic beams and can be size, isomer, and quantum state selected by means of electric deflection. These samples are then strongly laser aligned by intense picosecond laser pulses and serve as a well-defined sample for electron diffraction experiments. Controlling the molecules' state and spatial orientation increases the amount of information contained in electron diffraction patterns.

The developed electron gun and first experiments will be presented.

MO 1.4 Mon 11:30 BEBEL HS213

Optimal Control of Vibrational Cooling

— ●DANIEL REICH and CHRISTIANE KOCH — Theoretische Physik, Universität Kassel, Heinrich-Plett-Str. 40, 34132 Kassel

Laser cooling of a molecule's internal degrees of freedom employing broadband optical pumping involves a timescale separation between laser excitation and spontaneous emission. Current approaches fail if the Franck-Condon map governing the optical transitions is preferential to heating rather than cooling. We show that by using optimal control theory to derive shaped pulses for the optical pumping step this issue can be circumvented entirely. To achieve this we have designed two different cooling schemes and corresponding optimisation functionals [1]. The optimised pulses drive population into those excited state levels that have the largest spontaneous emission rates to the target state while accumulating population in the ground state and keeping the cooling cycle loss-free. Our optimisation functionals are also applicable to the laser cooling of other degrees of freedom provided the cooling cycle consists of coherent excitation and dissipative deexcitation steps whose timescales are separated.

[1] D.M. Reich and C.P. Koch, *New J. Phys.* (to be published)

MO 1.5 Mon 11:45 BEBEL HS213

Cryogenic buffer-gas cooling: comparison of two different regimes

— ●XING WU, THOMAS GANTNER, SOTIR CHERVENKOV, MARTIN ZEPPENFELD, and GERHARD REMPE — Max-Planck-Institut für Quantenoptik, Hans-Kopfermann-Str. 1, D-85748 Garching, Germany

Cryogenic buffer-gas cooling is a promising method for producing bright beams of cold polar molecules [1] for low-temperature collision experiments, chemical reactions, and precision measurements. In combination with the electrostatic guiding technique [2], high-intensity beams of slow and low-field-seeking molecules can be extracted and delivered to further experiments. To optimize the flux of the guided beam, we investigate the performance of buffer-gas cooling in two different regimes, the effusive and the supersonic one. In the effusive regime, molecules with a low peak velocity and a high flux are obtained after the electric guiding. The velocity spread in this case corresponds to the temperature of the cryogenic cell. In the supersonic regime, molecules move at faster forward velocities, but are further cooled in the co-moving frame because of the adiabatic expansion. The output efficiency of the buffer-gas cell is also increased due to the hydrodynamic enhancement. However, the electric guiding of the supersonic beams has only limited performance, most likely because of collisions happening at the entrance of the electric guide, due to the large densities of both buffer gas and molecules in the forward beam.

[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 1.6 Mon 12:00 BEBEL HS213

Deceleration of SrF molecules in a traveling wave Stark decelerator

— ●JOOST E. VAN DEN BERG¹, SREEKANTH MATHAVAN¹, CORINE MEINEMA¹, JANKO NAUTA¹, KLAUS JUNGSMANN¹, HENDRICK L. BETHLEM², and STEVEN HOEKSTRA¹ — ¹University of Groningen, Groningen, The Netherlands — ²LaserLab, Department of Physics and Astronomy, VU University Amsterdam, The Netherlands

We present the first results on the deceleration of SrF molecules in a traveling wave Stark decelerator. Traditional Stark decelerators suffer from overfocusing, leading to losses. This makes it very inefficient to use such a device for the deceleration of heavy diatomics, such as SrF. A long traveling wave decelerator, which is inherently stable, is therefore built in our lab. Using arbitrary waveform generators and high voltage amplifiers we can create true 3D moving electric traps inside the decelerator. After deceleration, we will laser cool the molecules to prepare them for a parity violation measurement. We report the status of the experiment and the possibilities of using different waveforms to optimize the deceleration process.

MO 1.7 Mon 12:15 BEBEL HS213

Shedding Far-off Resonant Light on Polar Paramagnetic Molecules

— ●KETAN SHARMA and BRETISLAV FRIEDRICH — Fritz-Haber-Institut der Max-Planck-Gesellschaft, D-14195 Berlin, Germany

Interactions with external electric, magnetic or optical fields provide

the chief means to manipulate the rotational and translational motion of neutral gas-phase molecules. All such methods rely on the ability to create directional states of molecules as only in said states are the molecular body-fixed multipole moments available in the laboratory frame. A far-off resonant optical field hybridizes and aligns the rotational states of an anisotropic molecule. These states occur as tunneling doublets of opposite parity and are quasi-degenerate at high optical field intensities. For polar molecules, these states can be efficiently coupled either by the electric dipole interaction with a superimposed electrostatic field or by the electric dipole-dipole interaction

arising between a pair of polar molecules. Thus, a weak static electric field can orient such molecules projecting up to 90% of the dipole moment on the static field direction. For polar paramagnetic molecules, a superimposed magnetic field causes a further parity-conserving hybridization of the molecule's rotational states, doubling the number of the tunneling doublets by removing the degeneracy arising due to the sign of projection of angular momentum on the collinear field axis. The triple field-combination offers a high efficiency and flexibility in amplifying molecular orientation.

MO 2: Clusters

Time: Monday 10:30–12:30

Location: BEBEL SR144

MO 2.1 Mon 10:30 BEBEL SR144

Infrared spectroscopy of doped silicon clusters — ●NGUYEN XUAN TRUONG, MARCO SAVOCA, ANDRÉ FIELICKE, and OTTO DOPFER — Institut für Optik und Atomare Physik, TU Berlin, Germany

Doped Si clusters are investigated with resonant infrared-ultraviolet two-color ionization (IR-UV2CI) combined with global optimization and DFT calculations. Neutral Si_mX_n clusters are irradiated with tunable IR light from a free electron laser before being ionized with UV photons from an F_2 laser. Resonant absorption of IR photons leads to an enhanced ionization efficiency for the neutral clusters and provides the size-specific IR spectra. Structural assignment of the clusters is achieved by comparing the calculated linear absorption spectra of the most stable isomers with experimental data. For Si_mC_n (with $m+n=6$), we found the systematic transition from chain like geometries for C_6 to 3D structures for Si_6 [1]. For further first row doped Si_6X (with $\text{X} = \text{Be}, \text{B}, \text{C}, \text{N}, \text{O}$) clusters, additional properties have been calculated, such as binding and ionization energies, and natural bond orbitals. All X dopant atoms in Si_6X have a negative net charge suggesting that Si atoms act as electron donors within the clusters. Moreover, the overall structures of Si_6X strongly depend on the nature of the dopant atom (size and valency). While for some of the most stable Si_6X clusters one Si atom in the original Si_7 structure is simply substituted ($\text{X} = \text{Be}, \text{B}, \text{C}$), other cases exhibit a completely different geometry ($\text{X} = \text{N}, \text{O}$).

[1] M. Savoca, A. Lagutschenkov, J. Langer, Dan J. Harding, A. Fielicke, O. Dopfer, *J. Chem. Phys.* **A 117**, 1158 (2013).

MO 2.2 Mon 10:45 BEBEL SR144

Vibrational Spectra and Structures of Silicon Hydride Cluster Cation — ●MARTIN ANDREAS ROBERT GEORGE, MARCO SAVOCA, JUDITH LANGER und OTTO DOPFER — IOAP TU Berlin, Germany

Silanes and their derivatives and ions are fundamental species in a variety of chemical disciplines. IR spectra of silicon hydride cluster cations Si_xH_y^+ produced in a supersonic plasma molecular beam expansion of SiH_4 , He, and Ar are inferred from photodissociation of cold Si_xH_y^+ -Ar/Ne complexes obtained in a tandem quadrupole mass spectrometer coupled to an electron impact ionization source and an octopole ion trap. In addition, the clusters are characterized in their ground electronic states by quantum chemical calculations to investigate the effects of ionization and Ar/Ne complexation on their geometric, vibrational, and electronic structure. We present initial results for Si_2H_6^+ [1], Si_2H_7^+ [2] and Si_3H_8^+ [3], which have complex potential energy surfaces, with low-energy isomers featuring unusual three-center two-electron (3c-2e) bonding. The IR spectrum of disilanium, Si_2H_7^+ , a fully H-passivated Si_2 core with a Si-H-Si bridge is described by a 3c-2e bond. The excess proton in the Si-H-Si bridge generates three additional fundamentals, which provide the fingerprint of the 3c-2e bond.

[1] M. Savoca, M.A.R. George, J. Langer and O. Dopfer, *Phys. Chem. Chem. Phys.* **15**, 2774-2781 (2013) [2] M. Savoca, J. Langer and O. Dopfer, *Angewandte Chemie* **125**, 1376 (2013) [3] M.A.R. George, M. Savoca, O. Dopfer, *Chem. Eur. J.* **19** 45 (2013)

MO 2.3 Mon 11:00 BEBEL SR144

Measuring the efficiency of ICD in neon- and in water clusters — ●MARKO FÖRSTEL¹, TIBERIU ARION², LASSE HARBO³, CHAO FAN ZHANG⁴, and UWE HERGENHAHN¹ — ¹Max-Planck-Institute for Plasmaphysics, Greifswald, 17491, Germany — ²University of Hamburg, CFEL, Luruper Chaussee 149, 22761 Hamburg, Germany — ³Dept. of Physics and Astronomy, Aarhus University, Aarhus, 8000, Denmark — ⁴Dept. of Physics and Astronomy, Uppsala University,

Uppsala, 75121, Sweden

In our contribution we focus on the measurement of the efficiency of intermolecular coulombic decay (ICD) in neon clusters and in water clusters.

Quite uniquely, our setup allows the quantitative determination of the efficiency of ICD relative to other competing channels. We introduce this technique and discuss the ICD efficiency after inner valence ionization in neon clusters, in water clusters and in clusters of heavy water.

By comparing the ICD efficiency in water and heavy water we can estimate the influence of the dynamics of the two systems on the ICD efficiency. Using these results we can obtain limits on the decay rate of ICD in large systems, i.e. water clusters with a mean size of $N < 60$.

MO 2.4 Mon 11:15 BEBEL SR144

Microsolvation of the Formanilide Cation (FA^+) in a Non-polar Solvent: Infrared Spectra of $\text{FA}^+\text{-L}_n$ clusters ($\text{L}=\text{Ar}, \text{N}_2$) — ●JOHANNA KLYNE¹, AUDE BOUCHET¹, MATTHIAS SCHMIES¹, MITSUHIKO MIYAZAKI², MASAOKI FUJII², and OTTO DOPFER¹ — ¹Institut für Optik und Atomare Physik, Technische Universität Berlin — ²Chemical Resources Laboratory, Tokyo Institute of Technology, Japan

The peptide linkage is an essential component in biochemical recognition processes since its geometry, depending on its local environment, defines the conformation of proteins. Elucidating the sequential microsolvation of peptides is therefore crucial for a full description of their behaviour in biological media. The stepwise microsolvation of cationic formanilide ($\text{FA}^+\text{-L}_n$) is characterized by IR spectroscopy of size-selected clusters generated in a molecular beam, combined with density functional calculations. Formanilide is the simplest aromatic molecule containing a peptide linkage ($-\text{NH}-\text{CO}-$). The observation of size- and isomer-specific NH stretch frequencies reveals the microsolvation of FA^+ in a nonpolar ($\text{L}=\text{Ar}$) and a quadrupolar ($\text{L}=\text{N}_2$) solvent. Such aromatic amides exhibit at least two competing binding sites for nucleophilic ligands, namely H-bonding to the acidic N-H group of the amide and π -stacking to the phenyl ring. The H-bound $\text{FA}^+\text{-L}$ dimer with L binding to the NH proton of the amide is the most stable isomer. Subsequent ligands are weaker bound to the aromatic ring (π -stacking). These results demonstrate an ionization-induced change of the preferred binding motif from π -stacking to H-bonding.

MO 2.5 Mon 11:30 BEBEL SR144

CO binding to small transition metal alloy clusters — DAVID YUBERO VALDIVIELSO¹, WIELAND SCHÖLLKOPF², and ●ANDRÉ FIELICKE¹ — ¹Institut für Optik und Atomare Physik, Technische Universität Berlin, Germany — ²Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

We report on first experiments performed with the new infrared Free Electron Laser at the Fritz-Haber Institute in Berlin. The intense and widely tunable (so far 400–2300 cm^{-1}) IR radiation from the FEL is used to obtain cluster size and composition selective IR spectra of CO complexes of metal alloy clusters via IR multiple photon dissociation. Investigating the binding of carbon monoxide to metal sites via vibrational spectroscopy is frequently used to characterize their electronic and structural properties. The activation of the C-O bond that is probed via the C-O stretching frequency highly depends on the nature of the metal, leading to a transition from molecular to dissociative chemisorption for the earlier transition metals. This is usually related

to the rise of the d band center towards the earlier transition metals that allows for a stronger interaction with the CO's $2\pi^*$ orbitals. For pure clusters of many transition metals the binding of CO and the influence of cluster size and charge is well studied. We here aim to obtain an understanding of the effects of alloying on the CO activation, using it as a gauge for the change in the electronic structure in terms of the d band level. Results are presented for small alloy clusters composed from Co and Mn atoms.

MO 2.6 Mon 11:45 BEBEL SR144

Gas Phase Vibrational spectroscopy of Messenger-tagged Aluminum Oxide Clusters Anions — ●MATIAS R. FAGIANI¹, XIAOWEI SONG¹, WIELAND SCHÖLLKOPF¹, SANDY GEWINNER¹, FLORIAN A. BISCHOFF², JOACHIM SAUER², and KNUT R. ASMIS^{1,3} — ¹Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany — ²Humboldt-Universität zu Berlin, Institut für Chemie, Brook-Taylor-Str. 2, D-12489 Berlin, Germany — ³Lehrstuhlvertretung am Wilhelm-Ostwald-Institut, Universität Leipzig, Linnéstr. 2, D-04103 Leipzig, Germany

Alumina structures of reduced dimensionality are of interest in astrophysics and atmospheric chemistry, as well as in nanostructured ceramic materials and solid catalysts. Little is known, experimentally, concerning the geometric structure of such clusters. Vibrational spectroscopy combined with electronic structure calculations provides more detailed insight into the geometric and electronic structure of these clusters.

Here, we present infrared photodissociation (IRPD) spectra of aluminum oxide cluster anions, focusing mainly on the fully-oxidized, electronic closed-shell clusters. The cluster anions are formed in a sputtering source. Mass-selected anions are trapped, cooled to cryogenic temperatures and messenger-tagged (D_2) in a buffer gas filled ion trap. Photodissociation spectra are measured from 400 to 1200 cm^{-1} with the widely tunable IR radiation of the free electron laser FHI FEL. The spectra are assigned and cluster structures are determined by comparison with the results of density functional calculations.

MO 2.7 Mon 12:00 BEBEL SR144

Optical Properties of Supported Size Selected Ag Clusters in the Small Size Limit studied by SHG spectroscopy — PHILIPP HEISTER, ●TOBIAS LÜNSKENS, ARAS KARTOUZIAN, MARTIN TSCHURL, and UELI HEIZ — Chair of Physical Chemistry, Department of Chemistry and Catalysis Research Center, Technische Universität München, Lichtenbergstraße 4, 85748 Garching, Germany

The optical properties of noble metal nanoparticles have received considerable interest in the past decades due to their Localized Surface Plasmon Resonance (LSPR). These collective oscillations of conduction band electrons can be described classically by extensions of Mie theory for particle diameters down to 2 nm. For particles consisting of only a few atoms, this classical description does not hold true anymore. Only a few experimental investigations of this small size limit are reported so far. In those studies the optical properties of metal clusters in the gas phase and metal clusters embedded in rare gas matrices were investigated.

We present Second Harmonic Generation spectra of mono-dispersed silver clusters (Ag_n, $n < 55$). These clusters were generated by a laser vaporization source, size selected by a Q-MS and soft-landed onto a SiO₂ target. Spectra of individual sizes were recorded under UHV conditions. The spectra reveal a clear size dependency, which is discussed by comparison with literature.

MO 2.8 Mon 12:15 BEBEL SR144

Surface Scattering of (CO₂)_n off Si(111)/SiO₂ — BO-GAUN CHEN and ●WOLFGANG CHRISTEN — Humboldt-Universität zu Berlin, Brook-Taylor-Straße 2, 12489 Berlin, <http://clusterlab.de>

Employing a pulsed high-pressure supersonic jet expansion and a dedicated setup for the experimental investigation of chemical processes occurring between neutral, van der Waals bound clusters and a solid surface¹, we report on the angular distribution of large CO₂ clusters scattered off a Si(111)/SiO₂ surface under ultrahigh vacuum conditions. Scattered particles are detected using time resolved mass spectrometry. A translator stage provides the possibility to sample both the incoming beam (target surface retracted) and to determine the angular and velocity distribution of scattered particles. Angular information is obtained by rotating the target surface, the velocity of scattered particles is determined by changing the distance between surface and mass spectrometer.

The presented studies cover a very broad range of cluster sizes, n , $5 \cdot 10^3 < n < 2 \cdot 10^5$ molecules per particle, and focus on the influence of source entropy, realized by accurately setting stagnation pressure and temperature. We observe an interesting dependence of the angular distribution of scattered CO₂ monomers on source conditions, i.e. the scattering angle seems to reflect the expansion path, allowing to distinguish between cluster condensation via expansion on the gaseous or on the liquid side of the critical point, and an intermediate regime where the expansion passes the metastable gas-liquid region.

¹ W. Christen, K. Rademann, *Rev. Sci. Instrum.* **77**, 015109 (2006).

MO 3: Chiral Systems (SYCS 2)

Time: Monday 14:00–16:00

Location: BEBEL HS213

Invited Talk MO 3.1 Mon 14:00 BEBEL HS213

Imaging the Absolute Configuration of a Chiral Epoxide in the Gas Phase — ●HOLGER KRECKEL¹, PHILIPP HERWIG¹, KERSTIN ZAWATZKY², MANFRED GRIESER¹, ODED HEBER³, BRANDON JORDON-THADEN¹, CLAUDE KRANTZ¹, OLDŘICH NOVOTNÝ^{1,4}, ROLAND REPNOW¹, VOLKER SCHURIG⁵, DIRK SCHWALM^{1,3}, ZEEV VAGER³, ANDREAS WOLF¹, and OLIVER TRAPP² — ¹Max-Planck-Institut für Kernphysik, 69117 Heidelberg — ²Organisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg — ³Weizmann Institute of Science, 76100 Rehovot, Israel — ⁴Columbia Astrophysics Laboratory, New York, NY, USA — ⁵Institut für Organische Chemie, Eberhard Karls Universität Tübingen

Chiral molecules exist in two different configurations which are non-superimposable mirror images of one another. The respective configurations are referred to as enantiomers. Most methods to distinguish between enantiomers rely on interactions with polarized light. However, to infer the underlying handedness of the molecular structure (the absolute configuration) from spectroscopic measurements is non-trivial. Here we present foil-induced Coulomb Explosion Imaging measurements of isotopically labeled dideuterooxirane (C₂H₂D₂O). Our experiments allow for the determination of the handedness of enantio-selected samples by direct imaging of individual molecular configurations [1]. Our method requires no quantum-chemical calculations, and it can be applied to small species like epoxides, where the chiral information is carried by light atoms exclusively.

[1] P. Herwig et al., *Science* **342**, 1084 (2013)

MO 3.2 Mon 14:30 BEBEL HS213

Enantiomer Identification of Mixtures of Chiral Molecules with Broadband Microwave Spectroscopy — ●V. ALVIN SHUBERT¹, DAVID SCHMITZ¹, DAVID PATTERSON², JOHN M. DOYLE², and MELANIE SCHNELL^{1,3} — 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 — ³The Hamburg Centre for Ultrafast Imaging, Universität Hamburg, Hamburg, Germany

The phenomenon that biochemical molecules are built almost exclusively from left-handed amino acids and right-handed sugars is known as the "homochirality of life". In nature and as products of chemical syntheses, chiral molecules often exist in mixtures that must be analyzed to identify the molecular components and measure the enantiomeric excesses (ee). We present a new method of differentiating enantiomeric pairs of chiral molecules in the gas phase.[1,2] It is based on broadband rotational spectroscopy and is a sum or difference frequency generation three-wave mixing process. The signal phase differs by pi radians between members of an enantiomeric pair and signal amplitude is proportional to the ee. This technique can also be applied to mixtures of chiral molecules and we present results on the analysis of mixtures of carvone, menthone, and carvomenthone.

[1] D. Patterson, M. Schnell, J. M. Doyle, *Nature* **2013**, 497, 475-477.

[2] V. A. Shubert, D. Schmitz, D. Patterson, J. M. Doyle, M. Schnell, *Angewandte Chemie International Edition* **2013**, DOI: 10.1002/anie.201306271

MO 3.3 Mon 14:45 BEBEL HS213

Measures for Multiphoton Photoelectron Circular Dichroism (PECD) — CHRISTIAN LUX¹, CHRISTIAN SARPE¹, THOMAS BAUMERT¹, and MATTHIAS WOLLENHAUPT² — ¹Universität Kassel, Institut für Physik und CINSaT, D-34132 Kassel — ²Carl von Ossietzky Universität Oldenburg, Institut für Physik, D-26129 Oldenburg, Germany

PECD describes the asymmetry in the photoelectron angular distribution (PAD) after ionization of randomly oriented chiral molecules in the gas phase with circularly polarized light. PECD was observed in one photon ionization using synchrotron radiation. Recently, we have measured PECD by femtosecond REMPI of camphor and fenchone molecules [1]. In our experiments strong contributions of higher-order Legendre polynomials were observed. To apply PECD as a sensitive analytical tool, quantitative measures to evaluate the experimental PECD data are required. For one photon ionization, parameters to characterize the asymmetry of the PAD based on the forward/backward asymmetries have been developed [2]. Although this method can be extended to the multiphoton case, we show that measures based on the forward/backward asymmetry are generally not sufficient to quantify the multiphoton PECD. We suggest a more general measure based on the decomposition of the PAD into their gerade and ungerade part. In addition, a measure to evaluate images from non-cylinder symmetrical PAD is introduced. These measures are evaluated on experimental multiphoton PECD data from camphor molecules.

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

[2] L. Nahon et al., *J Chem Phys* 125, 114309 (2006).

Invited Talk

MO 3.4 Mon 15:00 BEBEL HS213

Circular Dichroism in Mass Spectrometry: Laser Pulse Induced Electron Wavepacket Dynamics — DOMINIK KRÖNER — Universität Potsdam, Institut für Chemie, D-14476 Potsdam, Germany

The qualitative and quantitative identification of chiral molecules is of central importance in chemical analysis. In mass spectrometry the distinction of enantiomers is achieved by applying circularly polarized laser pulses. The sample is ionized via multiphoton excitation induced by shaped ultrashort laser pulses of opposite helicity, which interact *enantiospecifically* with the chiral molecules according to their handedness. The resulting differences in the ion yields allow to determine a circular dichroism in the mass spectrum. The polarization is, however, not the only pulse parameter which influences the circular dichroism in the ion yields, but also e.g. the pulse duration or the wavelength [1].

We study the fundamental processes, which lead to the distinction of chiral molecules in mass spectrometry, by performing laser driven quantum electron dynamics based on *ab initio* electronic structure calculations, in particular TD-CIS(D). For that purpose, a full treatment of the electric field-electric dipole (and quadrupole) as well as magnetic field-magnetic dipole interactions is required [2]. The influence of different laser pulse parameters on the detected circular dichroism is investigated, in order to explain experimental observations and to allow for predictions of an optimal distinction of enantiomers.

[1] P. Horsch, G. Urbasch, K.-M. Weitzel, D. Kröner, *Phys. Chem. Chem. Phys.* **13**, 2378 (2011).

[2] D. Kröner, *J. Phys. Chem. A* **115**, 14510 (2011).

MO 3.5 Mon 15:30 BEBEL HS213

Characterisation and Control of Cold Chiral Compounds — CHRIS MEDCRAFT^{1,2,3}, THOMAS BETZ^{1,2,3}, V. ALVIN SHUBERT^{1,2,3}, DAVID SCHMITZ^{1,2,3}, and MELANIE SCHNELL^{1,2,3} — ¹Max-Planck-Institut für Struktur und Dynamik der Materie — ²Center for Free-Electron Laser Science — ³The Hamburg Centre for Ultrafast Imaging, Hamburg, Germany

A high-resolution, cavity-based Fourier-transform microwave spectrometer is being commissioned in Hamburg. It is based around the COBRA design (Coaxially Oriented Beam-Resonator Arrangement [1]) and consists of a semi-confocal arrangement of a planar mirror and a spherical curved mirror (diameter=0.6m, R=2m). The high resolution (ca. 3kHz) and larger spectral range (6-40GHz) of this instrument will complement our chirped-pulse FTMW spectrometer [2] (2-8.5GHz), 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 CpReNOCOL. We also present a method [4] that can distinguish between enantiomers by measuring a phase shift in a 3-wave mixing signal that is caused by the opposing signs of the product of the dipole moment components (μ_a, μ_b, μ_c).

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

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

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

[4] Patterson, Schnell & Doyle *Nature* 497(2013) 475

MO 3.6 Mon 15:45 BEBEL HS213

Tracing photoinduced enantiomeric excess by femtosecond accumulative spectroscopy — ANDREAS STEINBACHER, PATRICK NUERNBERGER, and TOBIAS BRIXNER — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

We utilize a fast and sensitive polarimeter [1], specifically designed for applications with femtosecond laser pulses, to follow the asymmetric photochemical conversion of a racemic mixture of 1,1'-binaphthyl-2,2'-diyl hydrogenphosphate. The photoreaction is initiated by circularly polarized UV laser pulses. Depending on the handedness of the polarization, more R- or S-enantiomers are gradually photodissociated, leading to a build-up of enantiomeric excess. Due to the sensitive accumulative detection scheme [1] with an interaction length of 250 μm and the measurement time set to 100 ms for a full determination of the optical activity, we are able to follow the dynamical evolution of this enantiomeric excess. For a specific illumination time, the enantiomeric excess is most pronounced, and decreases again for continued exposure to UV light, as a direct consequence of the different extinction coefficients of the enantiomers. Hence, this detection scheme gives rise to the possibility of employing it in quantum control applications in future experiments.

[1] A. Steinbacher, J. Buback, P. Nuernberger, and T. Brixner, *Opt. Express* 20, 11838 (2012).

MO 4: Theory 1: Molecular Dynamics

Time: Monday 14:00–16:00

Location: BEBEL SR144

Invited Talk

MO 4.1 Mon 14:00 BEBEL SR144

Ultracold Rydberg plasma formation in intense laser-cluster interactions: resolving the mystery of highly charged ions — THOMAS FENNEL — Institute of Physics, University of Rostock, Rostock, Germany

Many strong-field cluster experiments have demonstrated the emission of atomic ions in extreme ionization stages of $q \geq 20$, e.g. in Ref [1]. This observation is commonly interpreted as a proof for ultraefficient light absorption in laser-induced nanoplasmas, e.g. through transient resonant plasmonic heating in near-infrared pulses. However, it can be shown that electron removal from the cluster during the laser pulse - this outer ionization is what one would intuitively require for ionization - is insufficient to explain observed average charge states [2]. Striking evidence for this apparent contradiction is given by recent FEL experiments on large Xe clusters [3]. Via molecular dynamics

(MD) simulations we show that (i) large clusters are only weakly outer ionized during laser excitation and (ii) relax to finite, ultracold Rydberg plasmas. Our explicit MD analysis reveals that DC-field induced frustrated recombination, i.e. field ionization of this peculiar cluster state in weak static external fields, is key to explaining the observed highly charged ions [4]. Routes for identifying Rydberg plasmas in clusters experimentally via electron spectroscopy will be proposed.

[1] T. Döppner *et al.*, *Phys. Rev. Lett.* **105**, 053401 (2010)

[2] T. Fennel *et al.*, *Phys. Rev. Lett.* **99**, 233401 (2010)

[3] T. Gorkhover *et al.*, *Phys. Rev. Lett.* **108**, 245005 (2012)

[4] C. Peltz, in preparation

MO 4.2 Mon 14:30 BEBEL SR144

A ring-polymer approach to electronically nonadiabatic dynamics within the mapping representation — JEREMY O. RICHARDSON and MICHAEL THOSS — Institut für Theoretische Physik

und Interdisziplinäres Zentrum für Molekulare Materialien, Friedrich-Alexander-Universität Erlangen-Nürnberg

A new method [1] based on an extension of ring-polymer molecular dynamics is proposed for the calculation of thermal correlation functions in electronically nonadiabatic systems for which the Born-Oppenheimer approximation is not valid. The ring-polymer dynamics are performed using a continuous-variable representation of the electronic states within the mapping approach, such that the electronic and nuclear degrees of freedom are treated on an equal footing. Illustrative applications of the method to models for nonadiabatic processes with two electronic states coupled strongly to a nuclear mode show good agreement with exact quantum results for the dynamics over short to moderate times and reveal a systematic improvement over the classical implementation of the mapping approach (single-bead limit). Being based on trajectories, the method scales well with the number of degrees of freedom and will be applicable to simulate certain nonadiabatic processes in complex molecular systems.

[1] J. O. Richardson and M. Thoss. *J. Chem. Phys.* **139**, 031102 (2013).

MO 4.3 Mon 14:45 BEBEL SR144

Coherent electron hole dynamics near a conical intersection — HENRY TIMMERS¹, •ZHENG LI^{2,3}, NIRANJAN SHIVARAM¹, ROBIN SANTRA^{2,3}, ORIOL VENDRELL², and ARVINDER SANDHU¹ — ¹Department of Physics, University of Arizona, Tucson, AZ, 85721 USA — ²Center for Free Electron Laser Science, DESY, Notkestraße. 85, D-22607 Hamburg, Germany — ³Department of Physics, University of Hamburg, D-20355 Hamburg, Germany

The motion of an electron hole (positive charge) across a molecule is vital for many chemical and biological phenomena. These quantum mechanical charge dynamics are mediated through complex electron-electron and electron-nuclear interactions. The investigation of such processes is challenging since it requires preparing and monitoring a coherent superposition of quantum states in the ionized molecule. We create a coherent hole wavepacket near a conical intersection in photoionized CO₂ and study the coupled nuclear-hole dynamics in real-time by employing a femtosecond extreme-ultraviolet (XUV) pump and near infrared (NIR) probe. We directly observe the oscillation of the electron hole density between σ and π character, driven by the coupled bending and asymmetric stretch vibrations of the molecule, and provide a detailed theoretical investigation of the observed phenomena. We find that the degree of electronic coherence for the electron hole motion decreases with time due to Coulombic interaction of the excited photoelectron with the ion and we measure the rate of this decohering process.

MO 4.4 Mon 15:00 BEBEL SR144

Angle-resolved coarse-grained approach for molecules with high rotational mobility — •THOMAS HEINEMANN¹, KAROL PALCZYNSKI², JOACHIM DZUBIELLA², and SABINE H. L. KLAPP¹ — ¹Institut für Theoretische Physik, Technische Universität Berlin, Hardenbergstr. 36, 10623 Berlin — ²Institut für Physik - Komplexe Systeme, Humboldt Universität Berlin, Newtonstr. 15, 12489 Berlin

Defining an effective potential from a statistical mechanics point of view states back to Kirkwood [1], who introduced the potential of mean force. For a two-molecule system it can be used as an effective pair potential, if the configuration entropy is removed. This entropy represents the number of atomic states for each macroscopic state. The resulting pair potential is temperature dependent.

A method is introduced, which is capable to calculate the angle-resolved effective pair potential using steered dynamics only. Results are compared to those from umbrella sampling. Constraints or restraints are only attached to the center of mass distance. In our investigations, we focused on coronene molecules, bearing no charges, as a benchmark system. The coarse-grained potential is then mapped onto a modified version of the Gay-Berne potential with minor improvements, such as contact distance [2]. A qualitative comparison between the all-atom and coarse-grained-fitted model is presented using many-particle simulations in the isotropic and hexagonal columnar regime.

[1] J. G. Kirkwood, *J. Chem. Phys.* **3**, 300 (1935).

[2] F. de J. Guevara-Rodríguez and G. Odriozola, *J. Chem. Phys.* **135**, 084508 (2011).

MO 4.5 Mon 15:15 BEBEL SR144

A New Efficient Method for Calculation of Frenkel Exciton Parameters in Molecular Aggregates — •PER-ARNO PLÖTZ¹, THOMAS NIEHAUS², and OLIVER KÜHN¹ — ¹Institut für Physik, Universität Rostock, D-18051 Rostock, Germany — ²Institut I - Theoretische Physik, Universität Regensburg, D-93040 Regensburg, Germany

The Frenkel exciton Hamiltonian models an aggregate as Coulomb-coupled monomers. In addition to the monomeric excitation energies the Coulomb coupling is an essential parameter for its description. It is shown that this coupling can be very efficiently calculated using time-dependent tight-binding based density functional theory (TD-DFTB), which offers a consistent way to describe the electronic structures of the monomers and the exciton coupling in the aggregate. Coulomb couplings are expressed in terms of self-consistently determined Mulliken transition charges, obtained in a sub-system-like formulation. This opens the possibility for a consistent on-the-fly determination of Frenkel exciton parameters in molecular dynamics simulations.

The performance of the method is studied by comparing to DFT-based calculations for a small test system of a formaldehyde oxime dimer. Applied to a perylene bisimide dimer it offers the possibility to explore the dependence of the Coulomb coupling on the intermolecular coordinates. This yields an interpretation of the observed biphasic aggregation (F. Fennel et al., *JACS* 2013, doi:10.1021/ja409597x).

MO 4.6 Mon 15:30 BEBEL SR144

Linear dimensionality reduction in reactive quantum dynamics using reduced intrinsic reaction coordinates — •JULIUS ZAULECK, SEBASTIAN THALLMAIR, MATTHIAS LOIPERSBERGER, and REGINA DE VIVIE-RIEDLE — Department Chemie, Ludwig-Maximilians-Universität München

The curse of dimensionality might be the most important obstacle for quantum dynamical calculations of molecules with more than only a few atoms. In the field of reaction dynamics this usually is approached by reducing the dimensionality of the problem. This reduction presents itself with some intrinsic problems, since one has to find dimensions which can be neglected without knowing the quantum dynamical propagation in full dimensions. A common method is to choose a number of internal coordinates which appear to describe most of the chemical reaction. Valuable information for this choice is often given by critical points along the reaction as well as the intrinsic reaction coordinate.

We present an alternative way by also using the intrinsic reaction coordinate and additional criteria to find a suited subspace of the full problem. Here it is demanded of the subspace to be a constant linear combination of the underlying Cartesian coordinates of the atoms. This pleasantly results in a diagonal kinetic energy operator. The subspace also has to be the best choice of all the analyzed subspaces. Possible criteria defining the quality of this choice will be presented along with examples.

MO 4.7 Mon 15:45 BEBEL SR144

Ultrafast Energy Transfer by Short and Intense THz Pulse — •PANKAJ KUMAR 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, Hamburg, Germany — ³Center for Ultrafast Imaging, University of Hamburg, 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.

Here, we investigated the response of liquid water to one-cycle, 200fs long THz pulses spectrally centered at about 100/cm⁻¹ (~3 THz). At an intensity of about 10E10 W/cm², the pulse transfers energy mostly to translational mode of the water monomers along the polarization axis of the electric field. In a time-scale of 500fs to 1ps the energy redistributes to hindered rotational modes first, and to intramolecular vibrations last. We also investigated the response of Phenol molecule to such THz pulse in vapor phase and in liquid water environment. This study implies that the energy supplied by the THz can potentially activate chemical processes long before the large amount of energy supplied leads to volume increase and vaporization of the medium. In this study, we have used CP2K package for Ab-Initio Molecular Dynamics.

MO 5: Posters 1: Electronic Spectroscopy, Photochemistry, Femtosecond Spectroscopy

Time: Monday 16:30–18:30

Location: Spree-Palais

MO 5.1 Mon 16:30 Spree-Palais

An improved potential scheme of the system $A^1\Sigma_u^+$ and ${}^1\Pi_u$ of Mg_2 — ●HORST KNÖCKEL, STEFFEN RÜHMANN, and EBERHARD TIEMANN — Quest und Inst. f. Quantenoptik, Leibniz Universität Hannover

We have been investigating the spectra of diatomic alkaline earth metal molecules since few years. The properties of the molecular $X^1\Sigma_g^+$ ground states in form of precise potential energy curves derived from such investigations are important in view of future applications of the corresponding atoms Mg, Ca and Sr for optical clocks. The ground states of Ca_2 , Sr_2 , and recently of Mg_2 have been characterized, and cold collision properties like scattering lengths have been given. Experimentally, the vapours of the alkaline earth metal diatomics, here Mg_2 , are produced in a heat pipe. Methods like conventional absorption spectroscopy employing the high resolution of a Fourier-Transform spectrometer (FTS) or dispersion by the FTS of fluorescence induced by a fixed frequency laser revealed rich spectra. The spectra are more detailed and the transition frequencies are more precise by a factor of about 3 compared to previous studies. We extend the range of known transitions substantially to higher vibrational levels of the upper $A^1\Sigma_u^+$ state. Moreover, yet unknown perturbations were identified. A model based on potential energy curves will be presented describing the excited $A^1\Sigma_u^+$ state with good precision, accounting also for the perturbations assuming a coupling by the close lying ${}^1\Pi_u$ state, for which a potential could also be derived.

MO 5.2 Mon 16:30 Spree-Palais

Two Photon Excitation Spectroscopy on Terrylene — ●TOBIAS STAUT and GREGOR JUNG — Biophysical Chemistry, Saarland University, Saarbrücken, Germany

Due to its excellent photostability, extinction coefficient and quantum yield, Terrylene is ideally suited for single-molecule experiments. Yet, as Terrylene is relatively rare and expensive, its chemical and nonlinear optical properties are mostly unexplored. In order to prepare further examinations we successfully assembled a two photon excitation (2PE) fluorescence spectrometer. Instead of single point measurements to acquire absolute values of the absorptivity σ_{2PE} , we use the slope of the fluorescence intensity versus the varying excitation intensity. Our setup with a pulsed Ti:Sa excitation laser allows measurements in the wavelength range from 750 nm to 860 nm. The symmetry of excited states can be determined by comparing different laser light polarizations to each other. The reliability of our measured absolute absorptivities was verified by a comparison of σ_{2PE} of Fluorescein, Rhodamine 6G, and Perylene with published results. In our setup, two different states of Terrylene in solution can be excited by 2PE. As a first step towards the single-molecule level we measured single point spectra of Terrylene in p-Terphenyl with a cw Ti:Sa excitation laser. Further experiments will include spectroscopic measurements on the single-molecule level in order to determine the 2PE tensor.

MO 5.3 Mon 16:30 Spree-Palais

Time-resolved studies on isolated NTCDA and NDCA — ●THIEMO GERBICH and INGO FISCHER — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany

In spite of numerous applications of 1,4,5,8-Naphtalene-tetracarboxylic-dianhydride (NTCDA) in organic electronics such as thin-film-transistors, studies of the electronic structure and the dynamics of the isolated molecule are still rare. In our experiment we apply picosecond time-resolved photoionization spectroscopy and observed NTCDA in a pulsed molecular beam. We present the first results of the electronic structure and show some time-resolved transients. In addition we present measurements of 1,8-Naphtalenedicarboxylic-anhydride (NDCA) which appears as a fragment of NTCDA and shows as well a picosecond dynamic.

MO 5.4 Mon 16:30 Spree-Palais

Electronic structure investigation on mono- and trinuclear transition metal complexes — ●ANNEKEN GRÜN¹, FABIAN DIETRICH¹, KIFAH SALIH¹, EZGI KECELI¹, SAEID FARSAPOUR¹, CHRISTIAN SARCHER², PETER ROESKY², WERNER THIEL¹, and MARKUS GERHARDS¹ — ¹TU Kaiserslautern, Fachbereich Chemie, Erwin-

Schrödinger-Str. 52/54, 67663 Kaiserslautern, Germany — ²KIT, Fachbereich Chemie, Engesserstr. 15, 76131 Karlsruhe, Germany

Absorption and emission spectra of mono- and trinuclear transition metal complexes in solution are recorded to investigate their electronic structure. Furthermore lifetimes of the excited states are determined by using the time correlated single photon counting (TCSPC) method. The results are compared with the one of the pure ligands and additionally a comparison with DFT calculations is performed. The structurally unique hexakis(μ^2 -3-phenylpyrazolato)trinickel(II) complex with diamagnetic nickel(II) centers is of special interest to form nonmetallic species by reacting with 3(5)-ferrocenylpyrazole which possesses six redox active ferrocenyl moieties^[1]. The absorption and fluorescence spectra of the trinuclear complex were obtained in solid state, whereas in solution degradation was observed. For the mononuclear dichlorido{[2-(3-pyrazolyl)phenyl]diphenylphosphine}nickel(II) complex two different fluorescence bands are observed. A focus on these systems is the analysis of a possible HCl elimination after photoexcitation.

[1] K. Salih et al. *Eur. J. Inorg. Chem.* 2013, 6049-6059.

MO 5.5 Mon 16:30 Spree-Palais

Single-Molecule Spectroscopy on π -Conjugated Oligomers and Polymers — ●SEBASTIAN BADERSCHNEIDER¹, ULLRICH SCHERF², JÜRGEN KÖHLER¹, and RICHARD HILDNER¹ — ¹Experimentalphysik IV and BIMF, Universität Bayreuth, Universitätsstrasse 30, 95447 Bayreuth — ²Fachbereich C - Mathematik und Naturwissenschaften & Institut für Polymertechnologie, Universität Wuppertal, Gauss-Strasse 20, 42097 Wuppertal

We employ low-temperature single-molecule fluorescence spectroscopy on a ladder-type oligo(para-phenylene) with two chemical repeat units, constituting a model system for a chromophore on a conjugated polymer. The oligomer spectra are compared to those of single chromophores of the corresponding ladder-type polymer with ≈ 80 repeat units. The profile of the electronic spectra of both single oligomers and polymers feature a narrow line with a width of 1 - 80 cm^{-1} (FWHM) that we attribute to the purely electronic transition (zero-phonon line, ZPL). For the oligomer the ZPL is accompanied by a weaker line at lower energy ($\approx 150 cm^{-1}$) that is ascribed to an intra-molecular backbone stretch mode coupling to the electronic transition. For the polymer, in contrast, this vibration is not detectable. Instead we identified a shoulder in the low-energy tail of the ZPL that arises from phonon modes of the surrounding matrix (mean phonon energy: $\approx 20 cm^{-1}$). For both systems the electron-phonon coupling strength to these low-energy ($< 200 cm^{-1}$) vibrational modes is weak with a Debye-Waller factor > 0.2 .

MO 5.6 Mon 16:30 Spree-Palais

Measuring and modeling the size and shape dependent electronic structure of diamondoid particles — ●JANA ULRICH, TOBIAS ZIMMERMANN, ROBERT RICHTER, THOMAS MÖLLER, and TORBJÖRN RANDER — Institut für Optik und Atomare Physik, Hardenbergstr. 36, 10623 Berlin, Deutschland

Diamondoids are a class of sp^3 -hybridised carbon nano-structures [1]. The first member is adamantane, which can be seen as the smallest possible diamond. Through structural modification of one or more adamantane units, a completely size selectable range of particles can be obtained [2]. We report on the electronic structure of certain such particles, investigated with valence photoelectron spectroscopy. In our studies we were especially interested in the size dependent change of the ionization potential [3]. In large nanoparticles such changes can be described by the quantum confinement theory [4]. As this model was developed for much larger structures (typically 3-50 nm), we explored whether it is applicable to predict the ionization potential of the few-atom samples of different geometries. The basic principles of the modeling and its results in comparison to the experimental data will be presented.

[1] H. Schwertfeger, A.A. Fokin and P. R. Schreiner, *Angew. Chem. Int. Ed. Engl.* **47**, 1022 - 36 (2008)

[2] A. A. Fokin et al., *J. Am. Chem. Soc.* **134**, 13641-13650 (2012)

[3] T. Zimmermann et al., *J. Chem. Phys.* **139**, 084310 (2013)

[4] L. E. Brus, *J. Chem. Phys.* **79**, 5566 (1983)

MO 5.7 Mon 16:30 Spree-Palais

Towards a Photoswitchable Matrix at the Single-Molecule Level — ●REGINA SCHMIDT¹, MARTTI PÄRS¹, TINA WELLER², MUKUNDAN THELAKKAT², and JÜRGEN KÖHLER¹ — ¹Experimental Physics IV and BIMF, University of Bayreuth, 95440 Bayreuth, Germany — ²Applied Functional Polymers, University of Bayreuth, 95440 Bayreuth, Germany

The demonstration of all-optical circuits, where photons replace electrons as signal carriers, is a long-standing challenge [1]. One approach is, to regulate molecular fluorescence as a function of external stimuli by controlling the efficiency of the energy transfer between a fluorescent chromophore and a bistable photochromic switch [2]. Here we investigate a matrix that is doped with photochromic dithienylcyclopentene (DCP) and into which perylene bisimide (PBI) fluorophores are embedded. The DCP molecules undergo a photo-induced transition between two isomeric states which allows to modulate the fluorescence intensity from the PBI as a function of the states of the DCP [3]. The control of the fluorescence from single PBI molecules is demonstrated.

- [1] Francisco M. Raymo, *Adv. Mater.* 14, 401 - 414 (2002)
 [2] M. Pärns, C. C. Hofmann, K. Willinger, P. Bauer, M. Thelakkat and J. Köhler, *Angew. Chem. Int. Ed.* 50, 11405 - 11408 (2011)
 [3] M. Irie, *Chem. Rev.* 100, 1685 - 1716 (2000)

MO 5.8 Mon 16:30 Spree-Palais

Evolution of Interatomic Coulombic Decay in the Time Domain — ●FLORIAN TRINTER¹, JOSHUA B. WILLIAMS¹, MIRIAM WELLER¹, MARKUS WAITZ¹, MARTIN PITZER¹, JÖRG VOIGTSBERGER¹, CARL SCHOBER¹, GREGOR KASTIRKE¹, CHRISTIAN MÜLLER¹, CHRISTOPH GOIHL¹, PHILLIP BURZYNSKI¹, FLORIAN WIEGANDT¹, TOBIAS BAUER¹, ROBERT WALLAUER¹, HENDRIK SANN¹, ANTON KALININ¹, LOTHAR PH. H. SCHMIDT¹, MARKUS SCHÖFFLER¹, NICOLAS SISOURAT², and TILL JAHNKE¹ — ¹Institut für Kernphysik, Goethe Universität, Max-von-Laue-Strasse 1, 60438 Frankfurt, Germany — ²Université Pierre et Marie Curie, UMR 7614, Laboratoire de Chimie Physique Matière et Rayonnement, 11 rue Pierre et Marie Curie, F-75005 Paris, France

During the past 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: the excitation energy is transferred (in many cases over long distances) 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 the first direct measurement of the temporal evolution of ICD using a novel experimental approach.

MO 5.9 Mon 16:30 Spree-Palais

Vibrationally Resolved Decay Width of Interatomic Coulombic Decay in HeNe — ●FLORIAN TRINTER¹, JOSHUA B. WILLIAMS¹, MIRIAM WELLER¹, MARKUS WAITZ¹, MARTIN PITZER¹, JÖRG VOIGTSBERGER¹, CARL SCHOBER¹, GREGOR KASTIRKE¹, CHRISTIAN MÜLLER¹, CHRISTOPH GOIHL¹, PHILLIP BURZYNSKI¹, FLORIAN WIEGANDT¹, ROBERT WALLAUER¹, ANTON KALININ¹, LOTHAR PH. H. SCHMIDT¹, MARKUS S. SCHÖFFLER¹, YING-CHIH CHIANG², KIRILL GOKHBERG², TILL JAHNKE¹, and REINHARD DÖRNER¹ — ¹Institut für Kernphysik, J. W. Goethe-Universität, Max-von-Laue-Strasse 1, D-60438 Frankfurt am Main, Germany — ²Theoretische Chemie, Universität Heidelberg, Im Neuenheimer Feld 229, D-69120 Heidelberg, Germany

We investigate the ionization of HeNe from below the He 1s3p excitation to the He ionization threshold. We observe HeNe⁺ ions with an enhancement by more than a factor of 60 when the He side couples resonantly to the radiation field. These ions are an experimental proof of a two-center resonant photoionization mechanism predicted by Najjari et al. [*Phys. Rev. Lett.* 105, 153002 (2010)]. Furthermore, our data provide electronic and vibrational state resolved decay widths of interatomic Coulombic decay in HeNe dimers. We find that the interatomic Coulombic decay lifetime strongly increases with increasing vibrational state.

MO 5.10 Mon 16:30 Spree-Palais

Fluorescence modulation of photochromic perylene bisimide dithienylcyclopentene triads: A quantitative model — ●MARTTI PÄRS¹, MICHAEL GRADMANN¹, REGINA SCHMIDT¹, KATJA

GRÄF², PETER BAUER², MUKUNDAN THELAKKAT², and JÜRGEN KÖHLER¹ — ¹Experimental Physics IV, University of Bayreuth, 95440 Bayreuth, Germany — ²Applied Functional Polymers, University of Bayreuth, 95440 Bayreuth, Germany

We present fluorescence modulation experiments using an organic photoswitchable triad that consists of a photochromic unit (dithienylcyclopentene, DCP) that can be interconverted between two bistable (open and closed) forms by light, and two highly efficient fluorophores (perylenebisimide, PBI) [1]. The experiments were carried out as a function of the intensities of the excitation beam that probes the fluorescence and the conversion beam that triggers the photocyclisation of the DCP. From the data we develop a kinetic model that allows us to predict quantitatively the degree of fluorescence modulation as a function of the mutual intensities of the two lasers.

- [1] M. Pärns, C.C. Hofmann, K. Willinger, P. Bauer, M. Thelakkat, J. Köhler, *Angew. Chem. Int. Ed.* 2011, 50, 11405-11408

MO 5.11 Mon 16:30 Spree-Palais

H⁺ + Cl⁻: Photoion pair production in HCl studied by bipolar three-dimensional (3D) photoion pair imaging — ●CHRISTOF MAUL¹, MIKHAIL PORETSKIY¹, ALEXEY CHICHININ², and KARL-HEINZ GERICKE¹ — ¹Institut für Physikalische und Theoretische Chemie, TU Braunschweig — ²Institute of Chemical Kinetics and Combustion, Novosibirsk, Russia

Ion pair production is one of several competing processes occurring in many molecules. It has been studied intensively by photoexcitation in the vacuum ultraviolet (VUV) wavelength range. Complementing these studies, we report a resonance enhanced multi-photon ionization (REMPI) technique using readily available UV light and 3D imaging in order to simultaneously monitor the oppositely charged ionic products.

The advantage of this approach is that we can exclusively address the photoion pair among numerous competing processes. Moreover, much larger portions of the relevant potential energy surfaces can be interrogated than in single photon VUV experiments. 3D distributions of fragment momentum vectors can be determined containing the complete information about the fragmentation process with kinetic energy and spatial fragment distributions or anisotropy parameters as subsets.

We demonstrate the method for HCl fragmentation as prototype because HCl is known for photoion pair production, and its fragmentation dynamics have intensively been studied. From our data, the existence of a Rydberg gateway state for photoion pair generation is verified. The approach can easily be applied to any molecule exhibiting a potential energy surface with attractive part at large internuclear distances.

MO 5.12 Mon 16:30 Spree-Palais

Anharmonic vibrational analysis and modeling of a proton transfer reaction of flavonoids in different electronic states — ●TOBIAS C. MARTIN¹, ANDREAS FUNK², ANKE STAMM¹, MARTIN WEILER¹, and MARKUS GERHARDS¹ — ¹TU Kaiserslautern, Fachbereich Chemie, Erwin-Schrödinger-Str. 52, 67663 Kaiserslautern — ²Present address: Universität Siegen, Institut für Bau- und Werkstoffchemie, Paul-Bonatz-Str. 9-11, 57076 Siegen-Weidenau

Coumarines and Flavonoids are organic dyes that occur e.g. in leaves and petals. They are known for their antioxidative and photoprotective effects by undergoing excited state intramolecular proton transfers (ESIPT). The explanation of this process requires detailed knowledge of the potential energy surfaces (PES) of the ground and the excited state. To describe the ESIPT of 3-hydroxychromone (3-HC) and 3-hydroxyflavone (3-HF) along the proton transfer coordinate, different models have been chosen. One-, two- and partly three-dimensional potential energy surfaces have been calculated at the density functional theory (DFT) level. For the excited state the calculations are based on time dependent density functional theory (TDDFT). From these models vibrational eigenvalues can be calculated and compared to the experiments, additionally the minimum energy pathways are discussed.

MO 5.13 Mon 16:30 Spree-Palais

Excited-state proton transfer in a pyranine-derived super-photoacid — ●JOHANNES KNORR¹, BJÖRN FINKLER², GREGOR JUNG², and PATRICK NUERNBERGER¹ — ¹Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg — ²Biophysikalische Chemie, Universität des Saarlandes, 66041 Saarbrücken

The phenomenon of photoacidity, i.e. an increase in acidity by some orders of magnitude upon electronic excitation, is frequently met in

aromatic alcohols capable of transferring a proton to a suitable acceptor [1]. We recently synthesized a promising new class of so-called super-photoacids and their methylated counterparts based on pyrene, and demonstrated the extent of solvent induced solvatochromic effects by means of changes in the respective absorption and emission spectra [2]. Aiming at deeper insights into the underlying mechanisms contributing to excited-state intermolecular proton transfer, we extend our study by scrutinizing the associated ultrafast dynamics employing transient absorption spectroscopy in combination with fluorescence detection. Specifically, we try to explore whether vibrational excess energy has any influence on the proton-transfer process.

[1] T. Förster, *Naturwissenschaften*, 1949, 36, 186-187

[2] C. Spies et al., *Phys. Chem. Chem. Phys.* 2013, 15, 19893-19905

MO 5.14 Mon 16:30 Spree-Palais

The role of excess energy in the ultrafast Wolff rearrangement and subsequent reactions of 5-diazo Meldrum's acid — ANDREAS STEINBACHER, •SEBASTIAN ROEDING, TOBIAS BRIXNER, and PATRICK NUERNBERGER — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

5-Diazo Meldrum's Acid (DMA), an α -diazocarbonyl used in photolithography, is known to show a rich wavelength-selective photochemistry upon UV irradiation [1,2]. Transient-absorption studies in the liquid phase revealed an ultrafast intramolecular Wolff rearrangement to a ketene after 267 nm excitation. For DMA in the gas phase, pyrolysis studies [3] postulate a proceeding reaction of the product ketene via a second Wolff rearrangement.

We compare the time-resolved photofragment ion signals of DMA in the gas phase for 267 nm and 200 nm pump wavelength. The probe step is performed by multiphoton ionization with an 800 nm pulse. A global fit of the ion transients with a sequential model allows us to discriminate the dynamics of the reaction intermediates. Our data identify the timescales for ketene formation and indicate a subsequent Wolff rearrangement of the ketene product for higher pump energies.

[1] A. Bogdanova, and V. Popik, *JACS* 125 (2003)

[2] P. Rudolf, J. Buback, J. Aulbach, P. Nuernberger, and T. Brixner, *JACS* 132 (2010).

[3] S. L. Kammula, H. L. Tracer, P. B. Shevlin, and M. Jones, *J. Org. Chem.* 42 (1977).

MO 5.15 Mon 16:30 Spree-Palais

CRASY Transition State — •CHRISTIAN SCHRÖTER and THOMAS SCHULTZ — Ulsan National Institute of Science and Technology, UNIST-gil 50, Ulsan 689-798, Republic of Korea

Correlated Rotational Alignment Spectroscopy (CRASY) correlates high-resolution rotational Raman spectra with observables from pump-probe ionization spectroscopy. The CRASY lab relocated from Germany to the Ulsan National Institute of Science and Technology (UNIST) in Korea. A specialized femtosecond laser system will allow us to resolve rotational Raman spectra with a sub-100 kHz frequency resolution. The poster will show CRASY results and will illustrate the technological basis for very high resolution CRASY experiments.

MO 5.16 Mon 16:30 Spree-Palais

Perturbed Polarization Decay and Line-Shape Modifications in Liquids — •KRISTINA MEYER, ZUOYE LIU, ANDREAS LUDWIG, CHRISTIAN OTT, ANDREAS KALDUN, MARTIN LAUX, THOMAS DING, and THOMAS PFEIFER — Max-Planck-Institut für Kernphysik, Saupfercheckweg 1, 69117 Heidelberg, Germany

Recent time-resolved absorption experiments in helium allowed the transformation of Fano to Lorentzian line shapes via laser control of the optical dipole response caused by phase changes in doubly-excited states [1,2]. Here, we study a generalization of this mechanism to more complex systems such as molecules in the liquid phase. We perform transient-absorption measurements in a solution of the dye IR144 in methanol using few-cycle, 7-fs NIR laser pulses in a compact, high-stability time-resolved spectroscopy setup [3]. Modifications of the absorption profiles can be observed as a function of the coupling laser intensity. In addition, a pulse shaper has been set up in combination with the multiphoton intrapulse interference phase scan method (MI-IPS) [4]. This provides the opportunity to characterize and control the shape of the interacting laser pulses and to explore the control of electronic states and their couplings by observing pulse-shape dependent line shapes in the future.

[1] C. Ott et al., arXiv:1205.0519 (2012)

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

[3] Y. Zhang, K. Meyer, C. Ott, and T. Pfeifer, *Opt. Lett.* 38, 356 (2013)

[4] B. Xu et al., *J. Opt. Soc. Am. B* 23, 750 (2006)

MO 5.17 Mon 16:30 Spree-Palais

Phase-modulated Pump-Probe Experiments with Alkali Atoms — •LUKAS BRUDER, SABRINA LIPPS, MARIO HENNE, MARCEL MUDRICH, and FRANK STIENKEMEIER — Physikalisches Institut, Universität Freiburg, Germany

In view of implementing a 2D spectroscopy setup at a molecular beam apparatus, we are investigating a phase-modulation technique established by Marcus *et al.* [1]. In this collinear arrangement of four fs laser pulses, acousto-optical phase modulation imparts an intensity modulation on the detected nonlinear fluorescence signal. Demodulated rephasing and non-rephasing signals can be extracted using a lock-in amplifier. This method effectively decouples the relative temporal phases from the pulse envelopes and provides a high S/N scheme.

Having implemented this method in a fs pump-probe geometry with a simple gas cell, we could confirm an excellent S/N quality, a wide tuneability and great spectral resolution. Currently, we are testing the applicability to a molecular beam apparatus in a pump-probe scheme. By performing measurements with atomic alkali beams we focus on the signal detection by photo ionization and the possible combination with VMI detection. An extension to doped helium nanodroplet experiments should yield more insight in alkali-droplet coupling mechanisms.

[1] P. F. Tekavec, G. A. Lott, and A. H. Marcus, *J. Chem. Phys.* 127, 214307 (2007)

MO 5.18 Mon 16:30 Spree-Palais

Photophysics of Pyrophosphito-bridged diplatinum complexes — •BENEDIKT BURGARD¹, FLORIAN BÄPPLER¹, PATRICK SINGER¹, FABIAN RUPP¹, ROLF DILLER¹, CHRISTOPH RIEHN², YEVGENYI NOSENKO², DIMITRI IMANBAEW², and SEBASTIAN KRUPPA² — ¹Dept. of Physics, Univ. Kaiserslautern, 67663 Kaiserslautern, Germany — ²Dept. of Chemistry, Univ. Kaiserslautern, 67663 Kaiserslautern, Germany

The binuclear platinum(II) complex [Pt₂(μ -P₂O₅H₂)₄]⁴⁻ (PtPOP) exhibits interesting ultrafast photoinduced dynamics^[1,2]. We employ fs transient absorption in the UV/Vis and mid-IR in solution and fs pump-probe photofragmentation (PF) of isolated anionic PtPOP species in gas phase, generated by electrospray ionization. Wavelength dependent PF studies provide information on electronic states and fragmentation behavior. Cooperative effects with respect to electronic and nuclear dynamics of M-PtPOP(-M) (M = Ag⁺, Tl⁺) species were studied. Wavepacket motion and transient IR spectra give information on structural dynamics. Solution experiments are compared to those in gas phase evaluating the influence of the solvent on energy relaxation processes (IC, ISC).

MO 5.19 Mon 16:30 Spree-Palais

Strong-field control of population transfer in laser dyes with designed femtosecond laser pulses — •TILLMANN KALAS¹, TOBIAS BLUMENSTEIN¹, JOHANNES SCHNEIDER¹, MATTHIAS WOLLENHAUPT², and THOMAS BAUMERT¹ — ¹Universität Kassel, Institut für Physik und CINSaT — ²Universität Oldenburg, Institut für Physik

We present control of the population transfer in commercially available laser dyes by resonant strong-field excitation with shaped near infrared femtosecond laser pulses. Working in the singlet system of the laser dyes, we investigate population control mechanisms discovered earlier in the triplet system of photosensitizer dyes [1] using our high precision pulse shaper [2].

To that end we record control landscapes with respect to the fluorescence intensity of the dyes by a systematic variation of laser pulse shapes combining second order and third order dispersion. In the strong-field regime, we find highly structured topologies with large areas of maximum or minimum population transfer. Furthermore, we compare our experimental results with simulations on generic molecular potentials by solving the TDSE for excitation with shaped pulses. We discuss our findings with respect to our previous work and the therein discovered control mechanisms. Within this context, we give an outlook on the application of strong field controlled fluorescence in the research field of nonlinear microscopy.

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

[2] J. Köhler *et al.*: *Opt. Express*, **19**(12), 11638(2011)

MO 5.20 Mon 16:30 Spree-Palais

Ultrafast non-radiative relaxation dynamics of electronically excited pentafluorobenzene by femtosecond time-resolved mass spectrometry — ●OLE HÜTER, HENDRIKJE NEUMANN, and FRIEDRICH TEMPS — Institut für Physikalische Chemie, Christian-Albrechts-Universität zu Kiel

The perfluoro effect in unsaturated aliphatic and aromatic hydrocarbons leads to a pronounced lowering of the $\pi\sigma^*$ electronic state located on the C-F bond. As a result, the $\pi\sigma^*$ state in pentafluorobenzene (PFB) becomes almost isoenergetic with the $\pi\pi^*$ excited state. We have studied the ultrafast non-radiative excited-state dynamics of jet-cooled PFB using femtosecond transient time-of-flight mass spectrometry. The molecules were excited by femtosecond pump pulses of 30 fs duration at selected wavelengths in the range 240–273 nm and probed by multi-photon ionization with 100 fs pulses at 800 nm. The observed temporal profiles exhibit a complex multi-exponential decay behaviour. Depending on the excitation energy, at least two and up to five decay time constants were necessary to fit the experimental data. These may be assigned to the transfer through the conical intersection between the S_1 and S_2 states, as well as the relaxation to the electronic ground state. The most prominent feature of all transients is a superimposed coherent oscillation with 75–78 cm^{-1} frequency and damping times between 0.8 and 6 ps, accounting for up to 40 percent of the total signal. In accordance with our previous work on HFB (Studzinski and Temps, JCP **128**, 2008), this might hint at the vibrational coupling mode between the two electronic states.

MO 5.21 Mon 16:30 Spree-Palais

Photophysics of a Trinuclear Palladium Complex: Experiment and Theory — ●1 FLORIAN BÄPPLER¹, PATRICK SINGER¹, BENEDIKT BURGARD¹, FABIAN RUPP¹, 1 YVONNE SCHMITT², MARKUS BECHERER², ANNEKEN GRÜN², ANOUK M. RIJS³, FLORIAN WALZ⁴, FRANK BREHER⁴, WIM KLOPPER⁵, ROLF DILLER¹, and MARKUS GERHARDS² — ¹Dept. of Phys. — ²Dept. of Chem., TU Kaiserslautern, 67663 Kaiserslautern — ³Faculty of Science, Radboud University Nijmegen, 6525 Nijmegen, The Netherlands — ⁴Inst. of Inorg. Chem., KIT — ⁵Inst. of Phys. Chem., KIT, 76131 Karlsruhe

A detailed knowledge of the involved excited states of metal complexes is essential for the manipulation or optimization of various functional properties. Important factors are their electronic distribution, molecular geometries, and pathways for relaxation and deactivation. Here we present a detailed theoretical and spectroscopic study on the electronically excited states of a trinuclear palladium complex in both gas phase and solution. The application of DFT and TDDFT methods as well as a variety of spectroscopic methods to the chosen complex $[\text{Pd}_3\{\text{Si}(\text{mt}^{\text{Me}})_3\}_2]$ leads to the first detailed analysis of the photophysics of a symmetric trinuclear complex. In combination with the calculations, energies, structures and lifetimes of the excited electronic states are characterized by applying the Resonant-2-Photon-Ionization method in a molecular beam experiment as well as luminescence, time-correlated single photon counting and excited state femtosecond absorption spectroscopy in solution. (1 = presenting authors)

MO 5.22 Mon 16:30 Spree-Palais

Temperature-Dependent Femtosecond Spectroscopy reveals Energy Barriers in Ultrafast Electronic Deactivation — ●UTA CORINNA STANGE and FRIEDRICH TEMPS — Institute of Physical Chemistry, Christian-Albrechts-University Kiel, Germany

The dissipation of excess electronic energy is of utmost importance to biological molecules such as the DNA to avoid photochemical damage. To understand the photophysical mechanisms of electronic deactivation of DNA building blocks detailed information on the involved potential energy surfaces (PES) is needed. While quantum chemical calculations become feasible for these molecules, the experimental characterization of specific features of the PES remains a challenge even for femtosecond spectroscopy.

Here we demonstrate a straightforward method to reveal local minima and energy barriers on deactivation pathways: temperature-dependent femtosecond time-resolved fluorescence spectroscopy. Our measurements of the DNA building blocks adenine (A) and its dinucleotide ($d(A_2)$) clearly show temperature-dependent behavior for their ultrafast electronic deactivations. Excited-state lifetimes decrease with increasing temperature indicating thermal activation. Observed activation energies can be assigned to shallow potential energy wells along the deactivation pathways of the excited states in the monomer and to excimer states in the dimer. The results allow us to quantify the depth of potential energy wells and barriers experimentally.

MO 5.23 Mon 16:30 Spree-Palais

Photoinduced Processes in a Low-Spin Cobalt(II) Semiquinonate Complex — ●FABIAN RUPP¹, KATHARINA CHEVALIER¹, ANNEKEN GRÜN², MANUEL ZIMMER², MARKUS GERHARDS², CHRISTOPH VAN WÜLLEN², HANS-JÖRG KRÜGER², and ROLF DILLER¹ — ¹Dept. of Physics, Univ. of Kaiserslautern — ²Dept. of Chemistry, Univ. of Kaiserslautern, 67663 Kaiserslautern

Metal complexes undergoing valence tautomerism (VT) and spin-crossover (SCO) by external stimuli may be utilized as novel molecular switches. Femtosecond UV/Vis-pump-UV/Vis- and mid-IR-probe-spectroscopy is employed to investigate the first cobalt(II) semiquinonate complex $[\text{Co}(\text{L-N}_4\text{tBu}_2)(\text{dbsq})](\text{B}(p\text{-C}_6\text{H}_4\text{Cl})_4)$, that displays temperature dependent SCO rather than VT [1]. Surprisingly after photo-excitation in resonance with a CT-band at 1075 nm we do not observe the transient formation of a catecholate species (VT) but instead two intermediate excited semiquinonate states with different high-spin configuration (SCO) and lifetimes $\tau_1 \approx 0.9$ ps and $\tau_2 \approx 9$ ps, respectively, and a complete ground state recovery on a picosecond time scale. The assignment of the transient high-spin species in the photocycle is based on quantum chemical calculations, static electrochemical, temperature dependent UV/Vis, mid-IR, Raman and resonance-Raman spectroscopy.

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

MO 5.24 Mon 16:30 Spree-Palais

Characterization of surface plasmon excitation using femtosecond pulses for ultrafast time resolved spectroscopy using a Kretschmann arrangement — ●ALIREZA MAZAHARI TEHRANI, FAEZEH MOHAGHEGH, MAHESH NAMBOODIRI, and ARNULF MATERNY — Research Center for Functional Materials and Nanomolecular Science, Jacobs University Bremen, Campus Ring 1, D-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). In our work, we would like to gain a better understanding of the coupling of the electronic systems of metal and adsorbate. For this, we use a Kretschmann configuration, which helps to characterize the interaction in a reproducible manner. So far, many investigations have been done in the frequency domain. However, in the time domain, due to the nature of the femtosecond pulses, the coupling of the ultrashort pulses to the surface plasmon could be different in nature and efficiency. Therefore, a precise characterization of this process is needed to ensure the correct interpretation of time resolved experiments. In our contribution, we present our preliminary results, which help to better understand the interaction of femtosecond laser pulses with the electrons of thin metal layers.

MO 5.25 Mon 16:30 Spree-Palais

Excited state of guanosine in water - a time-resolved photoelectron study — ●FRANZISKA BUCHNER and ANDREA LÜBCKE — Max-Born-Institute Berlin, Germany

Interaction of ultraviolet light with DNA molecules may lead to photodamage and consequently may cause development of cancer. Upon excitation, natural DNA bases reveal ultrafast relaxation mechanisms that prevent photodamage.

We studied the time-resolved photoelectron spectrum of guanosine (the nucleoside of the DNA base guanine) in liquid water. Sub-100 fs pulses of 266 nm or 238-248 nm excite an 1 mmolar buffered solution of guanosine. The relaxation of the resonantly excited state is probed by photoionization using delayed ultrashort UV pulses of different photon energies. The kinetic energy distribution of the photoelectrons resembles the time-dependent binding energy of the excited state. Due to the broad absorption band of guanosine, also the probe pulse induces dynamics (negative temporal direction). From the comparison of the results for different pump wavelength, we can derive information about the role of higher lying excited states.

Additional information is derived from the one-colour multi-photon ionization, when only the pump or the probe pulse is present. We will describe and interpret in detail the photoelectron spectra in terms of the excited state dynamics of guanosine.

MO 5.26 Mon 16:30 Spree-Palais

Two Photon Absorption in Organic Molecules — ●BAIDAA HAMED — FU-Berlin

We have applied a combination of two techniques to measure two-

photon absorption (TPA) cross-sections and TPA-spectra of organic molecules in solution. One method is based on the measurement of the change in the transmittance. The sample scanned along the focused pump-beam. By another approach, we used the same pump configuration, but we measured the efficiency of fluorescence induced due to TPA. As a pump source we used Ti-sapphire laser providing 150 fs pulses at 780 nm and at a repetition rate of 1 kHz. The laser was used to carry the measurements (0,3 -5 mW power), or to pump an home-built optical parametric amplifier (OPA) tunable in the range of 1050-1400 nm. Tested measurements and a calibration of our system were done by measuring TPA cross-sections at 780 nm in Rhodamine 6G, Coumarin 47 and corroles dissolved in methanol at typical concentration of 6 mM/l. Fitting the transmittance and fluorescence efficiency versus the sample position and the pump-beam intensity enables to determine TPA cross-section. We have done preliminary measurements in some photosensitizer molecules, which are important for photodynamic therapy. This research is in progress.

MO 5.27 Mon 16:30 Spree-Palais

Molecular frame electron diffraction imaging with ultrashort electron pulses — ●FARUK KRECINIC, JEAN-GABRIEL BRISSET, ARNAUD ROUZÉE, and MARC VRAKING — Max-Born-Institut für Nichtlineare Optik und Kurzzeitspektroskopie, Berlin, Deutschland

Following ultrafast molecular dynamics in real time and space is a long-standing goal in ultrafast science. We are developing a new ultrashort pulsed electron source setup in order to follow such ultrafast structural dynamic of molecules in the gas phase. The electron source will generate pulses with a bunch duration down to 100 fs and with an energy of 100 keV. These electrons will then be used to ionize molecules that have been pre-aligned with ultrashort laser excitation, producing energetic secondary electrons. Our experiment will focus on following changes in the molecular structure by looking at the angular momentum distri-

bution of the secondary electrons. This is predicted to display electron diffraction effects that can be linked to the structure of the molecule. Here we will show some first results of field-free alignment of the CF₃I molecule and its ionization with the electron source.

MO 5.28 Mon 16:30 Spree-Palais

Ultrafast vibrational and structural dynamics in water solutions of macrocycle hosts and iodine — ●MEHDI MOHAMMAD KAZEMI, PATRICE DONFACK, MAHESH NAMOBODRI, and ARNULF MATERNY — School of Engineering and Science, Jacobs University, Campus Ring 1, D-28759 Bremen, Germany

The formation of supramolecular architectures offers several possibilities to visualize new structural and dynamical properties of small guest molecules restrained within well-defined environments. Molecules confined within the restrained space of mesoporous materials display interesting properties in general and this aspect has been widely studied and exploited. Meanwhile the ability of a single, so-called macrocycle, to embody another molecule (i.e., at the molecular level) has attracted particular interest. Several ultrafast molecular responses are associated with some degree of nonlinearity in the medium concerned. It can happen that simply the molecular assembling, such as aggregation in solution and the formation of host-guest complexes with geometry restriction, as discussed in the present contribution, can lead to or notably influence nonlinear processes in the medium. In the present contribution, ultrafast vibrational and structural dynamics in water solutions of macrocycle hosts and iodine are discussed. Especially, we have observed different Kerr effect dynamics in the presence of cucurbituril macrocycles (with or without iodine) in water. We also discussed the characteristics of ultrafast transient absorption dynamics of iodine trapped inside cucurbituril macrocycles in comparison with the results obtained in cyclodextrins and zeolite nanocrystals.

MO 6: Femtosecond Spectroscopy 1

Time: Tuesday 10:30–12:15

Location: BEBEL HS213

Invited Talk MO 6.1 Tue 10:30 BEBEL HS213

Time-resolved absorption studies of photoinitiator molecules in solution — ●ANDREAS-NEIL UNTERREINER¹, HANNA A. ERNST¹, THOMAS J. A. WOLF¹, DOMINIK VOLL², ELENA FRICK², and CHRISTOPHER BARNER-KOWOLLIK² — ¹Institute of Physical Chemistry, Karlsruhe Institute of Technology (KIT), 76128 Karlsruhe, Germany — ²Institute for Chemical Technology and Polymer Chemistry, Karlsruhe Institute of Technology (KIT), 76128 Karlsruhe, Germany

Understanding early-time dynamics of photo-induced polymerization can be important for successful high-tech applications. This also implies the development of search criteria for molecules showing e.g. efficient triplet radical initiation processes. In this context, it is important to accurately determine the efficiency for both radical formation after photo-excitation and polymerization of formed radicals. In this contribution, focus is given on the elucidation of the first steps particularly with regard to radical formation by reporting new results of type-I (radical formation after α -cleavage) photoinitiators. It will be shown that ultrafast intersystem crossing (ISC) on a picosecond timescale is one crucial process towards adequately describing polymerization efficiency although the relevant timescales (ISC and radical polymerization) differ by many orders of magnitude. In combination with time-dependent density functional theory (TD-DFT) calculations and pulsed laser polymerization with subsequent electrospray ionization mass spectrometry (PLP-ESI-MS) for post-mortem analysis of the polymerization products, one can obtain a more detailed picture of the relevant pathways of some recently published photoinitiator molecules.

MO 6.2 Tue 11:00 BEBEL HS213

A comparative study on chirped-pulse upconversion and direct multichannel MCT detection — ●JOHANNES KNORR, PHILIPP RUDOLF, and PATRICK NUERNBERGER — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

We present a comparative study on two spectroscopic techniques employed to detect ultrafast absorption changes in the mid-infrared spectral range, namely direct multichannel detection via HgCdTe (MCT) photodiode arrays and the newly established technique of chirped-pulse

upconversion (CPU) [1,2]. Whereas both methods are meanwhile individually used in a routine manner, we directly juxtapose their applicability in femtosecond pump-probe experiments based on 1 kHz shot-to-shot data acquisition [3]. Additionally, different phase-matching conditions in the CPU scheme for a given mid-infrared spectrum are examined, thereby simultaneously detecting signals which are separated by more than 200 cm⁻¹.

[1] K. J. Kubarych et al., *Opt. Lett.* 2005, 30, 1228-1230

[2] K. F. Lee et al., *Opt. Express* 2009, 17, 18738-18744

[3] J. Knorr et al., *Opt. Express* 2013, 21, 30693-30706

MO 6.3 Tue 11:15 BEBEL HS213

Ultrafast dynamics of asymmetric trihalides – Which bond breaks? — ●SEBASTIAN SCHOTT, ANJA HASENKOPF, FLORIAN KANAL, PATRICK NUERNBERGER, and TOBIAS BRIXNER — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

Trihalides are very successful model systems for ultrafast time-resolved spectroscopy. These molecules allow detailed theoretical treatments, due to their small size, while providing pronounced dynamic observables. Especially triiodide I₃⁻ has been studied extensively with ultrafast spectroscopy in solution, e.g. by Ruhman [1] and Vöhringer [2]. The special feature of the asymmetric trihalides IBrCl⁻, I₂Br⁻, I₂Cl⁻ and Br₂Cl⁻, compared to the well-known symmetric triiodide, is the existence of two distinguishable chemical bonds. Therefore, the existence of two different diatomic fragments after photodissociation (e.g. IBrCl + $h\nu$ → IBr + Cl or ICl + Br) is in principle possible. We use transient absorption spectroscopy with supercontinuum white-light probe pulses to investigate possible reaction paths 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] T. Kühne, P. Vöhringer, *J. Chem. Phys.* 1996, 105, 10788

MO 6.4 Tue 11:30 BEBEL HS213

Ultrafast UV-induced photoisomerization of intramolecu-

larly H-bonded β -diketones — ●PRAMOD KUMAR VERMA, PATRICK NUERNBERGER, and TOBIAS BRIXNER — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

The chelated enol form (H-bonded) of β -diketones usually exhibits strong absorption bands in the UV region originating from the dipole-allowed $\pi\pi^*$ transitions ($S_2 \leftarrow S_0$). The photochemistry following the $\pi\pi^*$ transitions can lead to multiple pathways (isomerization, tautomerization, fragmentation) and is highly sensitive to the environment of the molecule. In the gas phase, the dominant pathway is fragmentation with the loss of an OH radical. In contrast, when β -diketones in solution are subjected to UV irradiation, isomerization is the main channel while no fluorescence is detected. The absence of fluorescence suggests the presence of very efficient non-radiative processes from the lowest excited singlet state. The aim of the present study is to understand the relaxation processes of simple β -diketones after excitation to the S_2 state in solution phase. Thus, the excited-state dynamics of β -diketones have been investigated using femtosecond transient absorption with broadband UV white-light detection. Our results confirm that the formation of the non-chelated conformers on electronic excitation of the chelated form occurs on an ultrafast time scale through a dark state. We propose a model that qualitatively explains the microscopic photochemical pathways based on all the experimental and theoretical data currently available.

MO 6.5 Tue 11:45 BEBEL HS213

IR-Vis Two-Photon Fluorescence Spectroscopy on Oxacine1 — ●FRANK FRIEDRISZIK and STEFAN LOCHBRUNNER — Universität Rostock, Institut für Physik, Universitätsplatz 3, 18055 Rostock

We present an infrared-excitation Raman-probe setup in the femtosecond-regime and demonstrate its potential by two photon absorption and time-resolved fluorescence measurements on a dye. A regenerative Ti:sapphire amplifier system generating ultrashort laser pulses at 800 nm serves as primary light source. One part of its output is spectrally narrowed by laser line filters and will be used as Raman-probe. Another part of the pump light is converted to in-

frared radiation by an optical parametric amplifier and a non-collinear difference frequency mixing stage. The time resolution of the setup is better than 700 fs as it was measured by sum frequency mixing of the IR and Raman-probe pulses.

In a first test experiment the fluorescence of the dye Oxacine1 is excited by two-photon absorption of the IR and probe light. The observed fluorescence dynamics with respect to the time delay between the IR and the probe pulse is discussed in the framework of vibrational redistribution processes.

MO 6.6 Tue 12:00 BEBEL HS213

S_2 to S_1 Relaxation Dynamics in Perylene Bisimide Aggregates and Monomers — ●STEFFEN WOLTER¹, FRANZISKA FENNEL¹, MARCO SCHRÖTER¹, FRANK WÜRTHNER², OLIVER KÜHN¹, and STEFAN LOCHBRUNNER¹ — ¹Institut für Physik, Universität Rostock, Universitätsplatz 3, 18055 Rostock — ²Institut für Organische Chemie und Center for Nanosystem Chemistry, Universität Würzburg, Am Hubland, 97074 Würzburg

In this contribution, the relaxation dynamics from the electronic S_2 state to the S_1 state of monomeric and aggregated perylene bisimide dyes are investigated by femtosecond pump-probe spectroscopy. The considered perylene bisimides are known for forming long J-aggregate chains at ambient conditions in which exciton migration and annihilation can occur. During the annihilation process, a transient population and fast relaxation of highly excited states is assumed. Therefore, the relaxation pathways of these highly excited states have to be investigated to understand the annihilation process itself.

To this end, ultrafast transient absorption measurements with excitation of the S_2 and the S_1 state are performed and compared to each other. After optical population of the S_2 state a delayed onset of the stimulated emission from the S_1 state is observed for the aggregate as well as for the monomer. This effect is induced by the S_2 to S_1 decay, which happens on an ultrafast time scale of less than 500 fs. The impact of aggregation on the S_2 to S_1 relaxation is discussed and the results are compared to theoretical predictions [1].

[1] Schröter M., Kühn O. *J. Phys. Chem. A* **117**, 7580 (2013)

MO 7: Experimental Techniques 1

Time: Tuesday 10:30–12:30

Location: BEBEL SR144

MO 7.1 Tue 10:30 BEBEL SR144

Räumlich aufgelöste TDLAS auf Basis angepasster tomographischer Algorithmen für die Erfassung von Ammoniakstrahlen im Abgasstrang eines Dieselmotors — ●SANI VAN DER KLEY¹, STEVEN WAGNER², FELIX STRITZKE² und VOLKER EBERT^{1,3} — ¹Reaktive Strömungen und Messtechnik, TU Darmstadt — ²Hochtemperatur Prozessdiagnostik, TU Darmstadt — ³Physikalisch-Technische Bundesanstalt, Braunschweig

Die zunehmende Verringerung der Emissionsgrenzwerte für Kraftfahrzeuge macht immer komplexere Abgasnachbehandlungsszenarien notwendig. Zur Minimierung von Stickoxiden in modernen Dieselfahrzeugen wird bei der selektiven katalytischen Reduktion (SCR) dem Abgas vor dem Eintritt in den Katalysator eine verdünnte Harnstofflösung zur Bildung von Ammoniak (NH_3) als NO_x -Reduktionsmittels zugeführt. Um eine Über- bzw. Unterdosierung des Harnstoffes zu vermeiden, sind neue Technologien zur Optimierung des Einspritzvorgangs notwendig. Zur Detektion der räumlichen Verteilung von Ammoniak vor und nach dem Katalysator wurde ein räumlich auflösendes Spektrometer auf Basis der Tunable Diode Laser Absorption Spectroscopy (TDLAS) realisiert. Als sogenannte „line-of-sight“ Messmethode, d.h. integrierende Messung der Konzentration entlang des Laserstrahls, ist die geeignete Anordnung mehrerer Laserstrahlen zur Realisierung einer räumlichen Auflösung notwendig. Wir stellen hier die Möglichkeiten zur räumlich aufgelösten TDLAS auf Basis angepasster tomographischer Rekonstruktionsalgorithmen für die in-situ Abgasdiagnostik vor und diskutieren deren Grenzen als auch Möglichkeiten.

MO 7.2 Tue 10:45 BEBEL SR144

Messung von absoluten NH_3 -Konzentrationen mittels fasergekoppelter TDLAS für die Abgasdiagnostik von Dieselmotoren — ●FELIX STRITZKE und STEVEN WAGNER — High Temperature Process Diagnostics, Technische Universität Darmstadt, Germany

In der Entwicklung von Abgasnachbehandlungssystemen der SCR-

Technik werden geringe Ammoniakkonzentrationen in heißer, korrosiver Umgebung üblicherweise durch Gasextraktion gemessen. Eine Alternative dazu bietet die Absorptionsspektroskopie mit durchstimmbaren Diodenlasern (TDLAS - *tunable diode laser absorption spectroscopy*), mit der u.a. absolute in-situ Spezieskonzentrationen mit hoher Zeitauflösung kalibrationsfrei gemessen werden können. Bei Verwendung mehrerer simultaner Messstrecken kann zusätzlich die räumliche Konzentrationsverteilung erfasst werden. Dazu wurde ein Spektrometer entwickelt, mit dem NH_3 -Konzentrationen bis zu einer Nachweisgrenze von 100 ppm mit einer zeitlichen Auflösung von 10 Hz bei Verwendung eines ~ 10 cm langen Absorptionspfades gemessen werden können. Erstmals wird hierbei ein fasergekoppelter DFB-Laser zur Messung von Ammoniak im $2,3 \mu\text{m}$ -Band verwendet und die Strahlung mittels eigens entworfener Faserdurchführungen minimalinvasiv in das Messvolumen eines generischen Abgasströmungskanal eingebracht.

Hierzu wird der Versuchsaufbau vorgestellt, Detaillösungen für die Faseranbindung erläutert, erste Messergebnisse präsentiert und die Charakteristika des Systems quantifiziert.

MO 7.3 Tue 11:00 BEBEL SR144

Coherent Anti-Stokes Raman Scattering Spectroscopy for the Chemical Analysis of Solutions from Miller-Urey Experiments — ●STEFAN GOMES DA COSTA¹, SABRINA SCHERER², ALBRECHT OTT², and ANDREAS VOLKMER¹ — ^{1,3} Physikalisches Institut, Universität Stuttgart, Stuttgart — ²Biologische Experimentalphysik, Universität des Saarlandes, Saarbrücken

Coherent anti-Stokes Raman scattering (CARS) spectroscopy has been demonstrated as a highly sensitive and chemically specific technique that enables the extraction of molecular components based on their intrinsic vibrational properties. Compared to spontaneous Raman or infrared spectroscopies, CARS offers higher detection sensitivity and is free of intrinsic background fluorescence. By exploiting these beneficial characteristics of CARS, here we demonstrate the chemical analysis

of solutions from Miller-Urey (MU) experiments, where low concentrations of unknown chemical constituents in the presence of strong auto-fluorescence background are to be analysed. Using a single-laser, broadband CARS excitation source, we demonstrate simultaneous acquisition of Raman signatures over a spectral range of more than 4000 cm^{-1} . Chemical species in the so-called fingerprint, the silent, and the CH-stretch regions were observed and classified. Furthermore, multi-photon induced fluorescence and UV absorption spectroscopies have been performed, and their results have been correlated with those of CARS spectroscopy. Our results demonstrate the high potential of CARS spectroscopy for the analysis of complex organic mixtures like MU primordial soups in the quest of the origin of life.

MO 7.4 Tue 11:15 BEBEL SR144

The microwave spectrum of the odd isotope of ytterbium fluoride, ^{171}YbF — ●JENS-UWE GRABOW¹, ZACHARY GLASSMAN², RICHARD J MAWHORTER², ANH LE³, and TIMOTHY C. STEIMLE³ — ¹Gottfried-Wilhelm-Leibniz-Universität, Hannover, Germany — ²Pomona College, Claremont CA, USA — ³Arizona State University, Tempe AZ, USA

Recent interest in the properties of ytterbium monofluoride, YbF , is primarily motivated by parity non-conservation (PNC) studies, and particularly the determination of electric dipole moment (e-EDM) of the electron, d_e . The advantages of utilizing heavy metal containing polar molecules like YbF for PNC measurements were recognized approximately 40 years ago and primarily stem from the very large obtainable internal electric fields, E^{int} , and the closeness of levels with opposite parity. The latter implies that the molecule can be fully polarized under application of a modest external field and the internal field realized is near the E^{int} value.

The pure rotational spectrum of a minor isotopologue of ytterbium fluoride, ^{171}YbF , in the $X^2\Sigma^+$ ($v=0$) state has been recorded using Fourier transform microwave (FT-MW) spectroscopy and pump/probe microwave optical double resonance (PPMODR) spectroscopy. The spectra were analyzed to produce an improved set of fine and hyperfine parameters for ^{171}YbF . Isotopic relationships and the determined ^{171}YbF parameters are used to predict the pure parameters and rotational transition frequency of ^{173}YbF .

MO 7.5 Tue 11:30 BEBEL SR144

Fibertest - Test for suitability of optical fiber feed-throughs and fibers in tritium atmosphere — ●KERSTIN SCHÖNUNG and SEBASTIAN SENST — Karlsruhe Institute of Technology (KIT), Institute of Technical Physics - Tritium Laboratory Karlsruhe (ITEP-TLK), Germany

Up to now the only possibility for tritium analytical methods, like FTIR-spectroscopy, to safely inject light into a glove box and a tritium system itself are optical windows bonded into vacuum flanges. Optical fiber feed-throughs and fibers could replace these windows and at the same time facilitate the setup.

But before fiber components can be used in a tritium system, two main questions have to be answered: Does tritium permeate through the fiber feed-through? Do optical properties change if the fiber is exposed to tritium? To answer these questions the Fibertest experiment is set up.

In this talk the setup and the measurement principle is explained. Furthermore the first results of the experiment are shown. This work is supported by the Carl-Zeiss-Foundation.

MO 7.6 Tue 11:45 BEBEL SR144

Accurate calibration of a Laser Raman system with (H,D,T) gas mixtures in thermodynamic equilibrium — ●SIMON NIEMES and MARCO RÖLLIG — Karlsruhe Institute of Technology, ITEP-TLK, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen

The Karlsruhe Tritium Neutrino (KATRIN) experiment aims to measure the neutrino mass via high-precision electron spectroscopy of the tritium beta decay with a sensitivity of $m_\nu = 200 \text{ meV}/c^2$ (90% C.L.).

This can only be achieved if systematic uncertainties are minimized. An important parameter is the isotopic composition of the gaseous beta electron source which is measured inline by Laser Raman spectroscopy. The KATRIN experiment requires a measurement trueness of better than 10% for the gas composition. Here we present a gas sampling technique for the calibration of the Raman system, with all hydrogen isotopologues (H_2 , HD, HT, D_2 , HT, DT, T_2). A tritium compatible loop will be set-up at the Tritium Laboratory Karlsruhe (TLK) to produce binary hydrogen gas mixtures in thermodynamic equilibrium and with well-known isotopic composition. Further analysis of the gas mixtures produced for the LARA calibration will be done by gas chromatography, mass spectroscopy and beta induced x-ray spectrometry.

MO 7.7 Tue 12:00 BEBEL SR144

Data Analysis for the TApIR Experiment — ●ALEXANDER KRAUS, ROBIN GRÖSSLE, and SEBASTIAN MIRZ — Karlsruhe Institute of Technology (KIT), Institute of Technical Physics (ITEP), Tritium Laboratory Karlsruhe (TLK)

Nuclear fusion reactors like ITER and DEMO require a fuel cycle with infrastructure for gas recycling. Part of this infrastructure is a facility that separates the six hydrogen isotopologues (Q_2) by cryogenic distillation. For this system, an inline, non-invasive method for real-time monitoring of the Q_2 concentrations is needed. The Tritium Absorption Infrared Spectroscopy (TApIR) experiment was deployed at the TLK in order to test the suitability of IR spectroscopy for this purpose.

With the experimental setup, Fourier Transform Infrared (FTIR) interferograms can be measured. Those interferograms are then processed by a software that applies a Discrete Fourier Transform (DFT). Results of the conventional data analysis in FTIR spectroscopy include transmission functions with a baseline different from one. For this reason, a Rolling Circle Filter (RCF) is included into the analysis procedure and optimized to remove this effect. From the resulting sample transmission functions, calibration quantities, like integrated absorbances, are then calculated. These can be used for a calibration with Q_2 concentrations, which are measured externally by an independent laser raman system, or, if a calibration exists, for the determination of Q_2 concentrations in unknown sample mixtures. In this talk, the different analysis steps will be presented and compared to the conventional analysis procedure in infrared spectroscopy.

MO 7.8 Tue 12:15 BEBEL SR144

IR spectroscopy on liquid hydrogen isotopologues with the Tritium Absorption Infrared (TApIR) experiment — ●SEBASTIAN MIRZ, ROBIN GRÖSSLE, and ALEXANDER KRAUS — Karlsruhe Institute of Technology (KIT), Institute of Technical Physics (ITEP), Tritium Laboratory Karlsruhe (TLK)

For the purification of the fusion plasma facilities like ITER and DEMO will circulate tritium and deuterium with a throughput of several kg per hour in their fusion fuel cycle. One important part of this fusion fuel cycle is the isotope separation system (ISS) using cryogenic distillation, which is under development at the Tritium Laboratory Karlsruhe (TLK).

The cryogenic distillation column of the ISS is able to separate mixtures of all six hydrogen isotopologues H_2 , HD, D_2 , HT, DT and T_2 . At the bottom of the cryogenic distillation column liquid tritium is accumulated. For monitoring the separation process, an inline and real-time analysis method able to measure the isotopologic concentration, is needed. As a test experiment for this analysis method the cryogenic sample cell of the TApIR experiment has been set up to simulate the conditions of the cryogenic distillation column. The TApIR experiment is able to liquefy hydrogen isotopologues at temperatures around 20 K and analyse them using infrared (IR) absorption spectroscopy. To deduce the gas composition from the recorded IR spectra calibration data of measurements with known mixtures is required. This talk will introduce the procedure for such a calibration measurement and present results with equilibrated inactive hydrogen isotopologue mixtures.

MO 8: Electronic Spectroscopy 1

Time: Tuesday 14:00–16:00

Location: BEBEL HS213

Invited Talk MO 8.1 Tue 14:00 BEBEL HS213
Selected Personal Highlights of Electron Collision Work —
 ●MICHAEL ALLAN — Department of Chemistry, University of Fribourg, Switzerland

The research in Fribourg is a continuation of the ingenious experiment of Franck and Hertz, the 100th anniversary of which we celebrate this year, as well as a continuation of later classical work of researchers like George Schulz or Helmut Ehrhardt. The talk will present a personal retrospective of few Fribourg experiments, performed in part in collaboration with the Kaiserslautern group of Hartmut Hotop, experiments which I believe the early pioneers would have appreciated. They will include older experiments where instrumental progress permitted insight into phenomena such as dipole-bound resonances, electron-driven proton transfer, or excitation of vibrational Fermi-resonances. More recent experiments where detailed information on the nuclear and autodetachment dynamics of temporary molecular negative ions is gained from 2-dimensional electron energy loss spectra will also be mentioned. Finally, some of the current trends of the electron collision field will be indicated.

MO 8.2 Tue 14:30 BEBEL HS213

Laser-assisted electron scattering in strong-field ionization of dense water vapor by few-cycle laser pulses — ●MARTIN WILKE, RUBA AL-OBAYDI, ALEXANDRE MOGUILJEVSKI, ALEXANDER KOTHE, JAN METJE, IGOR YUREVICH KIYAN, and EMAD FLEAR AZIZ — Joint Ultrafast Dynamics Lab in Solutions and at Interfaces (JULiq) Helmholtz-Zentrum Berlin, Albert-Einstein-Str. 15, 12489 Berlin and Freie Universität Berlin, FB Physik, Arnimallee 14, 14195 Berlin, Germany

Strong-field ionization of dense water gas was studied by means of angle-resolved time-of-flight electron spectroscopy. In contrast to diluted gases where above-threshold ionization (ATI) and high-order ATI (HATI) of single molecules dominate electron emission a collective effect of radiation absorption by neighboring particles known as laser-assisted electron scattering (LAES) was observed. This study was realized irradiating the vicinity of a liquid-microjet in a high vacuum chamber by 8-cycle near-infrared (1450 nm) laser pulses. Due to this combination strong-field photoelectron spectroscopy at liquid interfaces under high vacuum condition was facilitated.

MO 8.3 Tue 14:45 BEBEL HS213

Molecular Electronic Imaging via Laser Tunnelling — ●CHRISTOPHER T L SMEENK¹, LADAN ARISSIAN², ALEXEI V SOKOLOV³, KEVIN F LEE^{1,3}, MICHAEL SPANNER¹, ANDRE STAUDTE¹, DAVID M VILLENEUVE¹, and PAUL B CORKUM¹ — ¹Joint Lab for Attosecond Science, Ottawa, Canada — ²University of New Mexico, Albuquerque, USA — ³Texas A & M University, College Station, USA

Photoionization by intense, infrared laser pulses occurs via a tunnelling process. The photo-electrons emitted in laser tunnelling provide insight into atomic and molecular orbitals, much in the same way that the tunnelling current in a scanning tunnelling microscope (STM) gives information about surfaces. Laser STM therefore provides an avenue to unite the Ångström scale spatial resolution of tunnelling with femtosecond temporal resolution of optical pulses, allowing for new kinds of microscopy on the sub-atomic length and time scales.

We use circularly polarized femtosecond laser pulses at 800 nm to control and image N₂, O₂, and benzene. A non-resonant pump laser pulse prepares a rotational wavepacket allowing us to align the molecular axis in the lab frame. A precisely timed probe pulse singly ionizes the aligned molecules. By recording the emitted photo-electron spectrum in the molecular frame of reference, we show how laser tunnelling probes the symmetry and local electron density in the highest-occupied-molecular-orbital. Our results on these prototypical Σ and Π bonded molecules suggest how a laser STM could be applied to image dynamics on the sub-atomic scale.

MO 8.4 Tue 15:00 BEBEL HS213

Orbital mixing and charge transfer in aqueous ferric and ferrous aqueous solutions — ●JIE XIAO, ISAAK UNGER, RONNY GOLNAK, BERND WINTER, NÚRIA LLOBERA VILA, MARVIN POHL, EDLIRA SULJOTI, and EMAD F. AZIZ — Department of Functional Materials in Solution, BESSY II, Helmholtz Zentrum Berlin, Berlin, Germany

Charge transfer processes in Fe³⁺ and Fe²⁺ aqueous solutions were

analyzed based on combined energy-resolved photon and electron detections following soft X-ray excitation and ionization of a liquid microjet in vacuum. From the Auger-electron spectra and X-ray emission spectra, we access the ultrafast electron delocalization between ionic solute and water solvent. Experimentally, iron-water interactions are unequivocally identified through strong and orbital-specific intensity variations of the resonant photoelectron (RPE) spectra, and we also discuss how RPE spectra correlate with the respective X-ray emission spectra. Different Auger-decay channels, involving valence electrons versus deeper bound electrons, and X-ray emissions were investigated to reveal the state-dependent charge delocalization in iron ionic aqueous solution. Fe³⁺(aq) is found to exhibit larger charge transfer than Fe²⁺(aq). Our experimental results will be discussed with the help of DFT calculations.

MO 8.5 Tue 15:15 BEBEL HS213

The effect of ligand field symmetry on charge transfer process: x-ray absorption and emission investigation on Fe L edge of iron porphyrins — ●MARVIN POHL, JIE XIAO, RONNY GOLNAK, KAAAN ATAK, CHRISTOPH SCHWANKE, EDLIRA SULJOTI, and EMAD AZIZ — Department of Functional Materials in Solution, BESSY II, Helmholtz Zentrum Berlin, Germany

Iron porphyrin is the central and functional part existing in many vital proteins in biological system. The iron ion is the actual active site catalyzing a variety of complicated chemical reactions in which the iron 3d orbitals are strongly involved. Soft X-ray spectroscopy is an ideal tool to probe local electronic structure, which has recently been implemented by our team for the investigation of applied materials in liquid phase. Two iron porphyrin complexes with different side groups, iron octaethylporphyrin chloride (FeOEPCL) and iron tetraphenylporphyrin chloride (FeTPPCL), dissolved in solvent dichloromethane (CH₂Cl₂) have been investigated in flow cell by x-ray absorption and emission spectroscopy on Fe L edge. Their liquid phase resembles the real situation in biological system. The different delocalization extents of the certain Fe 3d orbital over the ligand N atoms under the x-ray excitation were revealed in the XAS and XES spectra of the two porphyrin molecules. The respective ligand field symmetry was found responsible for the various Fe 3d orbital overlapping with the ligand N 2p orbital in these two molecules which plays a significant role in the charge transfer process.

MO 8.6 Tue 15:30 BEBEL HS213

Dissociative photoionization of 1,4-di-tert-butyl-1,4-azaborine — ●FABIAN HOLZMEIER¹, MELANIE LANG¹, PATRICK HEMBERGER², and INGO FISCHER¹ — ¹Institut für Physikalische und Theoretische Chemie, Julius-Maximilians-Universität Würzburg, Am Hubland Süd, 97074 Würzburg, Deutschland — ²Swiss Light Source, Paul-Scherrer-Institut, 5232 Villigen PSI, Schweiz

Boron containing organic molecules play an important role for applications in optoelectronics and biomedicine. By synthesizing a 1,4-azaborine derivative, 1,4-di-tert-butyl-1,4-azaborine, inorganic chemists have found a synthetic route for an interesting, novel class of molecules. In an iPEPICO-experiment (imaging Photoelectron Photoion Coincidence) at the Swiss Light Source the photoionization of 1,4-di-tert-butyl-1,4-azaborine was investigated using VUV synchrotron radiation. The ionization energy of this molecule could be determined by threshold photoelectron spectroscopy, as well as the energetics of excited states in the cation. In addition, dissociative photoionization (DPI) was observed at higher photon energies. Several parallel and sequential dissociation channels were identified. The appearance energies of the fragment ions yield information on the chemical bonding. Using a RRKM rate theory approach the experimental data on the DPI to the three most important channels was modeled and accurate appearance energies were determined.

MO 8.7 Tue 15:45 BEBEL HS213

Threshold Photoionization of the 2-methylallyl radical — ●MELANIE LANG¹, FABIAN HOLZMEIER¹, INGO FISCHER¹, and PATRICK HEMBERGER² — ¹Institut of Physical and Theoretical Chemistry, Am Hubland Süd, D-97074 Würzburg, Germany — ²Molecular Dynamics Goup, Paul Scherrer Institut (PSI), CH-5232 Villigen PSI, Switzerland

Small radicals like 2-methylallyl are supposed to be reactive interme-

diates in combustion processes. Combustion-relevant molecules can be detected by photoionization in flames on-line. To assign a structure requires the knowledge of the ionization energy (IE) of the investigated reactive species. For this purpose we created 2-methylallyl by vacuum flash pyrolysis from 2-bromo-3-propene.

We obtained a gas phase TPES (threshold photoelectron spectrum) with an adiabatic IE of 7.88 eV for the singlet cationic state with several vibrational bands. Furthermore we detected the triplet cation at 9.55 eV, 1.67 eV above the adiabatic ionization energy.

MO 9: Theory 2: Molecular Dynamics & Quantum Chemistry

Time: Tuesday 14:00–16:00

Location: BEBEL SR144

MO 9.1 Tue 14:00 BEBEL SR144

Simulation of time-resolved pump-probe IR spectra — ●MATTHIAS WOHLGEMUTH and ROLAND MITRIC — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Würzburg, Deutschland

We present a new approach for the simulation of time-resolved pump-probe infrared (TRIR) spectra based on the molecular dynamics (MD) "on-the-fly". The simulations are carried out in the frame of density functional theory and have been combined with the Wigner phase space approach for the simulation of pump-probe spectra.

Our method was applied to the C=O to N-H water migration motion around a peptide linkage, which is observed by experimental TRIR spectroscopy. Our simulations reproduce all details of the measured time-resolved infrared spectra. The simulations show two concurrent mechanisms involved in the migration process, which were previously not derived from conventional stand-alone MD simulation and the simple experimental interpretation based on classical rate-equation analysis.

Altogether, our methods are uniquely suitable for the simulation of TRIR spectra in complex systems and provide a valuable help in the interpretation of the state-of-the-art experiments and it emphasizes the importance of the theoretical validation of TRIR experiments.

MO 9.2 Tue 14:15 BEBEL SR144

Nonlinear Absorption Dynamics Using Field-Induced Surface Hopping: Zinc Porphyrin in Water — ●MERLE I. S. RÖHR¹, JENS PETERSEN², and ROLAND MITRIC² — ¹Fachbereich Physik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin — ²Institut für Physikalische und Theoretische Chemie, Julius-Maximilians-Universität Würzburg, Am Hubland, 97074 Würzburg

The field-induced surface hopping (FISH) method [1] for the simulation and control of light-induced nonadiabatic dynamics in complex systems will be introduced and applied to the investigation of nonlinear absorption processes [2]. For this purpose, a systematic comparison of the FISH approach with exact quantum dynamics simulations on a multistate model system is provided, and it is demonstrated that FISH allows for accurate simulations of nonlinear excitation processes including multiphoton electronic transitions. The applicability of our method to complex molecular systems is illustrated by simulating the linear and nonlinear laser-driven dynamics in zinc (Zn) porphyrin in the gas phase and in water. To this end, the FISH approach is connected with the quantum mechanical-molecular mechanical approach (QM/MM) [2] which is generally applicable to large classes of complex systems. Our findings that multiphotonic processes increase the population of higher excited states of Zn porphyrin in the nonlinear regime provides a means for manipulating excited-state properties, such as transient absorption dynamics and electronic relaxation.

1. R. Mitric et al., Phys. Rev. A 79, 053416 (2009).
2. M. I. S. Röhr et al., ChemPhysChem 14, 1377 (2013).

MO 9.3 Tue 14:30 BEBEL SR144

Protein long timescale simulations using kinetic Monte Carlo — ●MATEUSZ MARIANSKI, CARSTEN BALDAUF, and MATTHIAS SCHEFFLER — Fritz-Haber-Institut der MPG, Berlin, Germany

The time scales that govern the structure formation and dynamics of biopolymers are hardly accessible with established molecular dynamics (MD) simulations. Too short simulation times may even lead to misinterpretation of the data, as previously shown for the dynamics of the amyloid beta peptide (Lin *et al.* *Biophys. J.* **2012**, 102, 315).

This project aims at the development of an universal kinetic Monte Carlo (kMC) protocol based on a separation of short- (bonded) and long-range (non-bonded) contributions as an alternative sampling technique applicable to peptides. Such kMC model of the structural dynamics of a molecule requires two components: (1) a library of accessi-

ble conformations, and (2) the transition states between these conformers. For the development, we turn to classical force fields, especially since we can compare to results from brute-force parallel-tempering MD sampling.

In this contribution, we will present results for polyaniline peptides of different lengths. The conformational library is constructed using structure-search algorithms and refined with clustering techniques. The resulting conformational basins are connected by transition states which later are used, by applying harmonic transition state theory, to estimate rates that are the input to the kMC simulation. Here we compare these results to brute-force sampling based on MD simulations to test the potential of such a protocol.

MO 9.4 Tue 14:45 BEBEL SR144

Non-Adiabatic Molecular Dynamics with Conditional Wave Functions — ●GUILLERMO ALBAREDA¹, HEIKO APPEL¹, IGNACIO FRANCO², ALI ABEDI³, and ANGEL RUBIO^{1,4} — ¹Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany — ²Chemistry Department, University of Rochester, USA — ³Max-Planck Institut für Mikrostrukturphysik, Germany — ⁴Nano-Bio Spectroscopy group and ETSF Scientific Development Center, Spain

A rigorous trajectory-based approach to treat the coupled electron-nuclear motion in terms of conditional wave functions is presented. By projecting the Schrödinger equation on the actual configuration of an infinite set of nuclear trajectories, an ensemble of conditional electronic equations of motion is obtained. These equations do not rely on any tracing-out of degrees of freedom and their propagation does not require a prior knowledge of the involved potential-energy surfaces. Using an exact factorization of the full molecular wave function, we establish a formal connection with the recently proposed exact potential energy surfaces [1]. This connection is used to gain insight from a simplified propagation scheme, which is demonstrated to capture non-adiabatic dynamics accurately in the limit of weak nuclear splitting. For pronounced branchings, we show how this simple algorithm partially captures dynamical steps between adiabatic surfaces [2] and discuss a route to improve the method. [1] A. Abedi, N. T. Maitra, and E. K. U. Gross, Phys. Rev. Lett. **105**, 123002 (2010). [2] A. Abedi, F. Agostini, Y. Suzuki, and E. K. U. Gross, Phys. Rev. Lett. **110**, 263001 (2013).

MO 9.5 Tue 15:00 BEBEL SR144

Temperature-Dependent Absorption Spectra of Molecular Aggregates: Influence of non-Markovian Environment — ●GERHARD RITSCHEL¹, WALTER T. STRUNZ², and ALEXANDER EISFELD¹ — ¹Max-Planck Institute for the Physics of Complex Systems, Dresden — ²Technical University Dresden

We investigate theoretically absorption spectra of complexes of chromophores interacting electronically via resonant transition dipole-dipole interactions. Often the electronic excitation couples to vibrational degrees of freedom in a strongly frequency-dependent way, leading to non-Markovian effects. We developed a new approach based on non-Markovian quantum state diffusion, with which it is possible to non-perturbatively calculate optical spectra. The approach explicitly takes the coupling to peaked spectral densities into account. The method is highly effective, allowing systematic investigations of large parameter spaces. We study absorption spectra of linear chains of identical monomers in the J-aggregate limit, and identify several distinct regimes for the temperature-dependent widths of these absorption spectra.

MO 9.6 Tue 15:15 BEBEL SR144

A route via X-ray emission spectroscopy for monitoring electron configuration during nuclear dynamics in excited molecules — ●HOSSEIN EBADI¹ and SIMONE TECHERT^{1,2,3} — ¹Structural dynamics of (bio)chemical Systems, MPI-BPC, Am

Fassberg 11, 37077 Goettingen, Germany — ²Structural dynamics of (bio)chemical Systems, DESY, Notkestrasse 85, 22607 Hamburg, Germany — ³Institute for X-ray physics, Goerg-August University, 37077 Goettingen, Germany

Core-hole spectroscopy, sensitive to the electron configuration of molecules and solids [1,2], has been traditionally used to get insight in the structure of matter from molecular to macroscopic scales. In this study, the main characteristics of azobenzene isomers, as a benchmark system for fundamental and applied studies in molecular electronics [3,4], are identified in the X-ray emission spectrum. The electron configuration has been examined using the shape of orbitals and via their contribution in the excited-state of UV-Vis regime. By applying an appropriate coordinate-to-time mapping [5,6], the change of electron configuration during the isomerization can be probed using time-resolved X-ray emission spectroscopy. [1] F. de Groot and A. Kotani, "Core level spectroscopy of solids", CRC Press, London, New York (2008). [2] I. Josefsson et al., J. Phys. Chem. Lett., 3, 3565 (2012). [3] J. M. Mativetsky et al., J. Am. Chem. Soc., 130, 9192 (2008). [4] A. Toniolo et al., J. Chem. Phys., 123, 234308 (2005). [5] H. Ebadi, C. H. Keitel, and K. Z. Hatsagortsyan, Phys. Rev. A, 83, 063418 (2011). [6] H. Ebadi, J. Opt. Soc. Am. B, 29, 2503 (2012).

MO 9.7 Tue 15:30 BEBEL SR144

A Relativistic Time-Dependent Density Functional study of the excited states of the mercury dimer — ●OSSAMA KULLIE — Institute for Physics, Department of Mathematics and Natural Science, Uni of Kassel. And Institute de Quantique Chimie, Uni Strasbourg, 4, rue de Blais Pascal, 67000 Strasbourg, France.

In this talk I present a time-dependent density functional (TDDFT) study for the ground-state as well as the excited states corresponding to the $(6s^2 + 6s6p)$, $(6s^2 + 6s7s)$ and $(6s^2 + 6s7p)$ atomic asymptotes for the mercury dimer Hg₂ [1]. I give analyze for its spectrum obtained from all-electron calculations performed with the relativistic Dirac-Coulomb and relativistic spinfree Hamiltonian. A comparison with the literature is given as far as available. Our result is excellent

for the most of the lower excited states and very encouraging for the higher excited states, it shows generally good agreements with experimental results and outperforms other theoretical results. This enables us to give a detailed analysis of the spectrum of the Hg₂ including a comparative analysis with the lighter dimers of the group 12, Cd₂ and Zn₂, especially for the relativistic effects, the spin-orbit interaction, and the performance of CAMB3LYP functional approximation and is enlightened for similar systems. [1] submitted to J. Chem. Phys. (2013).

MO 9.8 Tue 15:45 BEBEL SR144

Exact factorization of the electron-nuclear wave function: Is the molecular Berry phase an artefact of the Born-Oppenheimer approximation? — ●SEUNG KYU MIN^{1,2}, ALI ABEDI¹, KWANG S. KIM², and E.K.U. GROSS¹ — ¹Max-Planck-Institut für Mikrostrukturphysik Weinberg 2, D-06120 Halle, Germany — ²Pohang University of Science and Technology, Korea

The Born-Oppenheimer (BO) potential energy surfaces (PESs) provide an intuitive picture to analyze and interpret molecular processes. In this context, conical intersections (CIs) of the BO PESs are particularly important. They provide pathways for radiationless relaxation processes within the BO framework. Berry phases may arise when the Hamiltonian of a system depends on a set of parameters. In the BO approximation, the electronic Hamiltonian depends parametrically on the nuclear positions. If the full wave function (WF) is approximated by a single product of an electronic BO WF and a single nuclear WF, the variational equation determining the latter contains a Berry-type vector potential. However, in experiment, CIs and the associated Berry phases do not appear directly. One wonders whether the specific topological feature of Berry phase is an artifact of the BO approximation or whether it can be found for the exact full WF as well. To address this question we employ the exact factorization of the full WF which leads to a rigorous definition of the Berry connection [1,2]. Using a numerical study of a simple model, we answer the question whether the appearance of CIs and Berry phases survives in the exact treatment. [1] arXiv cond-mat/0502433 [2] PRL 105,123002 (2005)

MO 10: Posters 2: Biomolecules, Energy Transfer, Clusters, Quantum Chemistry, Molecular Dynamics and Chirality

Time: Tuesday 16:30–18:30

Location: Spree-Palais

MO 10.1 Tue 16:30 Spree-Palais

Polarization-resolved fluorescence-excitation spectroscopy of individual chlorosomes from the *bchR* - and *bchQR* - Mutant of *Chlorobaculum tepidum* — ●LISA MARIA WOHLRAB¹, MARC JENDRNY¹, DONALD A. BRYANT², and JÜRGEN KÖHLER¹ — ¹Experimental Physics IV and Bayreuth Institute of Macromolecular Research (BIMF), Universität Bayreuth, Universitätsstr. 30, 95447 Bayreuth, Germany — ²Department of Biochemistry & Molecular Biology, The Pennsylvania State University, 107 Althouse Lab, University Park, PA 16802

Chlorosomes are the main light-harvesting antennae complexes in green photosynthetic bacteria and contain bacteriochlorophyll *c*, *d* or *e* depending on the species. The chromophores self-assemble into aggregates without the involvement of a protein scaffold, and are organized in rods of 100 nm - 200 nm length and 20 nm - 50 nm width. For the species *Chlorobaculum tepidum* mutants (*bchR* and *bchQR*) have been prepared. The mutations affect the side groups of the BChl molecules.

Polarization resolved fluorescence-excitation spectroscopy on individual mutated chlorosomes reveal the importance of the methylation at C-8² position of the bacteriochlorophylls for the spectral properties of the chlorosomes.

MO 10.2 Tue 16:30 Spree-Palais

Broadband Microwave Spectroscopy of Biologically Relevant Complexes in the Gas Phase — ●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

Molecular recognition plays an important role in nature and is often very sensitive to small changes in the geometric structure. To learn more about molecular recognition we want to study systems which

mimic the cell recognition in the protein lectin, where the carbohydrates on a cell surface interact with the aromatic moieties of the protein. We want to study the importance of weak interactions, such as CH/ π interactions, for this recognition process. Therefore we will focus on interactions between aromatic molecules such as tryptophan and monosaccharides such as glucose. In particular, we want to compare slightly different recognition partners to get information about the influence of functional groups, steric effects or the molecular forces, which are involved.

We use Chirped-Pulse Fourier-Transform Microwave spectroscopy (CP-FTMW) combined with a supersonic jet to study the molecular complexes. It allows us to record the rotational spectrum from 2 - 8.3 GHz within a single acquisition. We also implemented a laser-ablation source that is crucial for our studies on these fragile molecules.

MO 10.3 Tue 16:30 Spree-Palais

Single-Molecule Fluorescence-Excitation Spectroscopy on LH2 Complexes from *Allochrochromatium Vinosum* — ●ALEXANDER LÖHNER¹, NICHOLA PICKEN², RICHARD COGDELL², and JÜRGEN KÖHLER¹ — ¹Experimental Physics IV, University of Bayreuth, Germany — ²Institute of Molecular, Cell & Systems Biology College of Medical Veterinary and Life Sciences, University of Glasgow, United Kingdom

The absorption spectrum of the high-light peripheral light-harvesting complex (LH2 complex) from the photosynthetic purple bacterium *Allochrochromatium vinosum* features two strong absorptions around 800 nm and 850 nm. In contrast to LH2 complexes from other species for the high-light LH2 complex from *Alc. Vinosum* the intriguing feature is that the B800 band is split into two components.

Fluorescence-excitation spectra of the B800 band from 71 single LH2 complexes have been registered. From that spectra it was possible to calculate the intra- and intercomplex spectral heterogeneity, and to ex-

tract the relative intensity and the homogeneous linewidth of the B800 absorptions. From this analysis and from the sum of the performed measurements we can rule out that the split of the B800 band comes from different types of LH2 complexes.

From comparison with computer simulations, we find the best agreement between simulation and experiment for a ring-like oligomer of 12 repeat units. The splitting of the B800 band can be reproduced if both an excitonic coupling between dimers of B800 molecules and their interaction with the B850 manifold is taken into account.

MO 10.4 Tue 16:30 Spree-Palais

Orientation dependence in $S^{14+} + He_2$ and $S^{14+} + Ne_2$ collisions at an impact energy of 11.37 MeV/u: Testing the impact parameter dependent ionization probabilities $P(b)$ of $S^{14+} + He$ and $S^{14+} + Ne$ collisions. — ●H. K. KIM¹, H. GASSERT¹, J. N. TITZ¹, M. WAITZ¹, J. VOIGTSBERGER¹, F. TRINTER¹, J. BECHT¹, A. KALININ¹, N. NEUMANN¹, C. ZHOU², L. PH. H. SCHMIDT¹, O. JAGUTZKI¹, A. CZASCH¹, M. SCHÖFFLER¹, H. MERABET³, H. SCHMIDT-BÖCKING¹, T. JAHNKE¹, H. J. LÜDDE¹, A. CASSIMI², and R. DÖRNER¹ — ¹University Frankfurt, Max-von-Laue-Str. 1, 60438 Frankfurt, Germany — ²CIMAP Caen, Bd Henri Becquerel, BP 55027 * 14076 Caen Cedex 05, France — ³Qatar University, P.O. Box: 2713 Doha, Qatar

We investigated the ionization of helium dimers (He_2) and neon dimers (Ne_2) by impact of very fast (11.37 MeV/u) S^{14+} projectile ions. We detect the Coulomb fragmenting ion pairs in the final charge states ($He^{1+} + He^{1+}$) and ($Ne^{n+} + Ne^{m+}$) with $(n,m) := (1,1), (2,1), (3,1), (2,2)$. The events were detected in an ion-ion-electron coincidence with the COLTRIMS technique. The measured three dimensional momentum vectors allow to also access the energies and the direction in which the particles propagate. Multiple ionization shows a strong dependence on the orientation of the dimer axis with respect to the projectile beam axis. These orientation effects are attributed to the impact parameter dependent ionization probabilities $P(b)$ for the atomic ionization processes $S^{14+} + He$ and $S^{14+} + Ne$. By comparing the data to a Monte Carlo simulation we test these atomic $P(b)$.

MO 10.5 Tue 16:30 Spree-Palais

Progress in imaging of ion molecule reactions — ●MARTIN STEI, EDUARDO CARRASCOSA, ALEXANDER DÖRFLER, ADITYA KELKAR, THORSTEN BEST, and ROLAND WESTER — Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck

Recent studies using our cross beam velocity map imaging (VMI) setup are presented. We have studied the reaction of F^- with CH_3Cl and have observed clear influence of the geometry of the transition state on the dynamics of the reaction, especially compared to our recent studies of the reactions of F^- and Cl^- with CH_3I [1,2]. We also report on our progress towards studying the influence of vibrational excitation of CH_3I on these reactions.

Furthermore we present the characterisation of three spatial map imaging modes of our 3D VMI spectrometer using multi-photon ionisation of toluene in a focused laser beam. A consistent analytical description of the imaging properties by a Taylor expansion has been applied and spatial resolution between 2 and $4 \mu m$ could be demonstrated [3].

[1] R. Wester, Phys. Chem. Chem. Phys. 16, 396 (2013) [2] J. Mikosch, J. Zhang, S. Trippel, C. Eichhorn, R. Otto, R. Sun, W. De-Jong, M. Weidemüller, W. L. Hase, R. Wester, J. Am. Chem. Soc. 135, 4250 (2013) [3] M. Stei, J. von Vangerow, R. Otto, A. H. Kelkar, E. Carrascosa, T. Best, R. Wester, J. Chem. Phys. 138, 214201 (2013)

MO 10.6 Tue 16:30 Spree-Palais

Measurement of the Autoionization Lifetime of the Energetically Lowest Doubly-Excited $Q_1^{1\Sigma_u^+}$ State in H_2 using Electron Ejection Asymmetry — ●ANDREAS FISCHER¹, ALEXANDER SPERL¹, PHILIPP CÖRLIN¹, MICHAEL SCHÖNWALD¹, SEBASTIAN MEUREN¹, JOACHIM ULLRICH², THOMAS PFEIFER¹, ARNE SENFTLEBEN¹, and ROBERT MOSHAMMER¹ — ¹Max-Planck-Institut für Kernphysik, Saupfercheckweg 1, 69117 Heidelberg, Germany — ²Physikalisch-Technische Bundesanstalt, Bundesallee 100, 38116 Braunschweig, Germany

Dissociative single ionization of H_2 induced by broadband XUV photons has been studied in a kinematically complete experiment. Emphasis is put on the asymmetry in the electron emission direction with respect to the outgoing H^+ -ion [1] as function of the excess-energies. The results are well reproduced by semi-classical model calculations that take into account interference effects along different dissociation

pathways [2]. We further present a way to use the measured asymmetry to disentangle the two contributing interfering pathways, direct ionization and autoionization. From this we are able to determine the autoionization lifetime of the energetically lowest doubly-excited $Q_1^{1\Sigma_u^+}(1)$ state for a large range of internuclear distances [3].

[1] Martín, F. et al. 2007 Science 315 5812

[2] Fischer, A. et al. 2013 PRL 110 213002

[3] Fischer, A. et al. 2013 J. Phys. B accepted

MO 10.7 Tue 16:30 Spree-Palais

Absolute configuration determination of a chiral epoxide using Coulomb Explosion Imaging — ●PHILIPP HERWIG¹, KERSTIN ZAWATZKY², MANFRED GRIESER¹, ODED HEBER³, BRANDON JORDON-THADEN¹, CLAUDE KRANTZ¹, OLDŘICH NOVOTNÝ^{1,4}, ROLAND REPNOW¹, VOLKER SCHURIG⁵, DIRK SCHWALM^{1,3}, ZEEV VAGER³, ANDREAS WOLF¹, OLIVER TRAPP², and HOLGER KRECKEL¹ — ¹Max-Planck-Institut für Kernphysik, Heidelberg — ²Organisch-Chemisches Institut, Ruprecht-Karls Universität Heidelberg — ³Department of Particle Physics and Astrophysics, Weizmann Institute, Israel — ⁴Columbia Astrophysics Laboratory, Columbia University, USA — ⁵Institut für Organische Chemie, Eberhard Karls Universität Tübingen, Tübingen

Molecules that exist in two configurations, which are non-superimposable mirror images of one another, are called chiral. It is well known that the handedness of a chiral molecule influences its reactivity with other chiral species. Nevertheless, the assignment of absolute handedness still proves a challenging task. Here, we present the first successful experimental determination of the absolute configuration of selected enantiomers in the gas phase, using foil-induced Coulomb Explosion Imaging [1]. Fast oxirane molecules were passed through a thin stripping foil, where the binding electrons are removed in sub-femtoseconds, causing the charged nuclei to repel each other strongly. The relative fragment velocities for individual molecular breakups were recorded and reveal the handedness of the molecules.

[1] Herwig et al., Science, Vol. 342, 1084-1086, 2013

MO 10.8 Tue 16:30 Spree-Palais

Imaging the structure of pure and isotopic helium trimers — ●JÖRG VOIGTSBERGER¹, STEFAN ZELLER¹, JASPER BECHT¹, NADINE NEUMANN¹, FELIX STURM^{1,2}, MAKSIM KUNITSKI¹, ANTON KALININ¹, JIAN WU^{1,3}, MARKUS SCHÖFFLER¹, WIELAND SCHÖLLKOPF⁴, DARIO BRESSANINI⁵, ACHIM CZASCH¹, KLAUS ULLMANN-PFLEGER¹, LOTHAR PH. H. SCHMIDT¹, ROBERT GRISENTI¹, TILL JAHNKE¹, and REINHARD DÖRNER¹ — ¹Universität Frankfurt a.M., Institut für Kernphysik, Frankfurt, Germany — ²Lawrence Berkeley National Laboratory, Chemical Sciences Division, Berkeley, USA — ³East China Normal University, State Key Lab of Precision Spectroscopy, Shanghai, China — ⁴Fritz-Haber-Institut der Max-Planck-Gesellschaft, Dep. of Mol. Phys., Atom and Molecule Optics, Berlin, Germany — ⁵University of Insubria, Department of Chemical and Environmental Sciences, Corno, Italy

We were able to measure the structure of 4He_3 and $^4He_2^3He$ by ionizing a jet of trimer clusters with a femtosecond Ti:Sa Laser. After expanding the gas through a precooled $5 \mu m$ nozzle, clusters of different mass were separated by a transmission diffraction grating. Ionization with a strong laser field led to a coulomb explosion of the trimer. In a ColTRIMS apparatus the 3d momenta of all ionized fragments were measured, giving a direct access to the structure of the trimer. Results are compared to recent theory.

MO 10.9 Tue 16:30 Spree-Palais

Experimental observation of the vibrational wavefunction of helium dimers using strong laser-fields — JÖRG VOIGTSBERGER¹, ●STEFAN ZELLER¹, JASPER BECHT¹, NADINE NEUMANN¹, FELIX STURM^{1,2}, MAKSIM KUNITSKI¹, ANTON KALININ¹, JIAN WU^{1,3}, MARKUS SCHÖFFLER¹, WIELAND SCHÖLLKOPF⁴, ACHIM CZASCH¹, LOTHAR PH. H. SCHMIDT¹, ROBERT GRISENTI¹, TILL JAHNKE¹, and REINHARD DÖRNER¹ — ¹Goethe Universität Frankfurt a.M., Institut für Kernphysik, Frankfurt, Germany — ²Lawrence Berkeley National Laboratory, Chemical Sciences Division, Berkeley, USA — ³East China Normal University, State Key Lab of Precision Spectroscopy, Shanghai, China — ⁴Fritz-Haber-Institut der Max-Planck-Gesellschaft, Dep. of Mol. Phys., Atom and Molecule Optics, Berlin, Germany

Helium gas is being expanded through a pre-cooled $5 \mu m$ nozzle in a supersonic gas jet at low temperatures. Containing small clusters this

gas jet passes a transmission diffraction grating, separating clusters of different masses. The first order dimer diffraction peak is overlapped with a femtosecond Ti:Sa Laser and ionised. The Coulomb exploding ionic fragments are measured with the COLTRIMS technique, giving direct access to the square of the vibrational wavefunction. The enormous size and the small binding energy can be directly accessed via this approach.

MO 10.10 Tue 16:30 Spree-Palais

Electrophilic and Nucleophilic Oxygen in Cationic Gold-Oxygen Cluster Complexes — ●ALEXANDER P. WOODHAM and ANDRÉ FIELICKE — Institut für Optik und Atomare Physik, Technische Universität Berlin, Germany

Clusters, small aggregates of atoms or molecules, exhibit properties which are often unique and unlike those of either the bulk material or the atom. One of the most well-known examples is that of gold clusters which, in contrast to the highly inert bulk phase, play part in a range of oxidation reactions utilizing molecular oxygen as a feed-stock. The origin for this change in reactivity is poorly understood and better characterization of the gold cluster complexes with oxygen may reveal structural or mechanistic details. Recent work has focused on the anionic and neutral clusters as the cationic clusters are thought to be unreactive towards molecular oxygen. In this poster, however, we present data for the binding and activation of molecular oxygen by cationic gold clusters. Spectroscopic characterization from infrared multiple photon dissociation spectroscopy (IR-MPD) allows determination of the oxidation state of bound oxygen molecules and unequivocally identifies the presence of both electron rich and electron poor adsorbates, even within the same cluster-complex composition.

MO 10.11 Tue 16:30 Spree-Palais

Vibrationally resolved fluorescence spectra of higher diamondoids — ●ANDREA MERLI¹, ROBERT RICHTER¹, CHRISTOPH HEIDRICH¹, RAMON RAHNER¹, TORBJÖRN RANDE¹, JEREMY DAHL², ROBERT CARLSON², JENS PETERSEN³, MERLE RÖHR³, ROLAND MITRIC³, and THOMAS MÖLLER¹ — ¹Institut für Optik und Atomare Physik, Technische Universität Berlin, Hardenbergstr. 36, 10623 Berlin, Germany — ²Stanford Institut für Materials and Energy Science, Stanford University, California, 94305, USA — ³Institut für Physikalische und Theoretische Chemie, Julius-Maximilians Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

Size and shape selected pristine diamondoids are optimal interaction-free systems for the investigation of electronic properties of molecular clusters in the gas phase. Vibrationally resolved emission spectra were obtained by exciting higher diamondoids with narrow band ultraviolet laser light. The origin of the spectra is found to be on transitions from the first electronically excited state into different vibrational modes of the electronic ground state. Quantum chemical calculations offer an accurate vibrational analysis of the diamondoids spectra making the assignment of the optically active normal modes possible.

MO 10.12 Tue 16:30 Spree-Palais

Characterizing the binding mechanisms of metal cluster-diamondoid hybrids — ●TOBIAS ZIMMERMANN¹, ANDRE KNECHT¹, ROBERT RICHTER¹, ANDREA MERLI¹, KONSTANTIN HIRSCH², TOBIAS LAU², THOMAS MÖLLER¹, and TORBJÖRN RANDE¹ — ¹Technische Universität Berlin, Berlin, Deutschland — ²Helmholtz-Zentrum für Materialien und Energie, Berlin, Deutschland

Metal cluster-diamondoid hybrid systems are expected to give new opportunities for studying electronic coupling mechanisms in tailor made nano scale semi-conductor systems. Diamondoids on one hand show shape and size dependent optical properties. Together with metal clusters which are mass selectable down to a size regime where every atom counts, they yield a broad range of parameters with which the electronic structure of the resulting hybrid system can be modified. First theoretical investigations hint at resonance effects for the optical and UV absorption region.

In this proof-of-principle study, we synthesized metal cluster-diamondoid hybrid systems and identified influences on the reactivity of metal clusters with (functionalized) diamondoids. Initial results, details of the experimental set-up and future extensions will be presented.

MO 10.13 Tue 16:30 Spree-Palais

IR and VIS spectroscopy on isolated ionic cobalt(ethanol) and nickel(ethanol) clusters — ●MARKUS BECHERER¹, TOBIAS C. MARTIN¹, ADAM KUBAS², WEI JIN³, GEORG LEFKIDIS³, KARIN FINK²,

WOLFGANG HÜBNER³, and MARKUS GERHARDS¹ — ¹TU Kaiserslautern, Fachbereich Chemie, 67663 Kaiserslautern — ²Karlsruher Inst. Technol., Inst. Nanotechnol., 76021 Karlsruhe — ³TU Kaiserslautern, Fachbereich Physik, 67663 Kaiserslautern

Investigations on clusters containing transition metals and aliphatic ligands provide the opportunity to study the differences between small molecular systems and nanoscaled particles. The successive aggregation of ligands (e.g. alcohol molecules) and their adsorption products on nickel-dimer-clusters are investigated in a molecular beam experiment. To obtain structural information about the (nickel)₂(ethanol)₁₋₃ cluster-cations and the (nickel)₂(ethanol)₁ anion the frequencies of the OH-stretching vibrations are probed by means of IR-photofragmentation spectroscopy. The structural assignment is performed by comparing the experimental data with calculated frequencies obtained from DFT calculations. The results give insight into both, the structure and reactivity of the nickel aggregates. In case of the isolated cationic (cobalt)₃(ethanol)₁ and (cobalt)₃(ethanol)₁(water)₁ clusters IR spectra as well as electronic spectra in the VIS region are investigated by applying photodissociation spectroscopy. The experimentally observed spectra serve as probe for theoretical calculations especially on the electronic transitions within the triangular Co trimer metal centre.

MO 10.14 Tue 16:30 Spree-Palais

Structural investigations on isolated 7-hydroxy-4-methylcoumarin aggregates in different electronic states by combined IR/UV spectroscopy — ●ANKE STAMM, MARTIN WEILER, KIRSTEN SCHWING, and MARKUS GERHARDS — Physikalische Chemie, TU Kaiserslautern, Erwin-Schrödinger-Straße 52, 67663 Kaiserslautern

Coumarin and its derivatives are well known for their photo-induced reactivity leading to their importance as photobiological and photochemical substances. 7-Hydroxy-4-methylcoumarin (7H4MC) for example was the first industrially used optical brightener. Thus the structural analysis of such photoreactive substances is of high scientific interest. For this purpose the application of combined double and triple resonance IR/UV methods in a molecular beam experiment is performed. These experimental techniques in combination with DFT calculations represent an ideal tool to investigate intrinsic structural preferences and rearrangements in the neutral electronic ground (S₀), excited state (S₁) as well as in the ionic ground state (D₀). The focus of the results presented here is on the tetra-, penta- and hexahydrate of 7H4MC which are of importance regarding the influence of a biologically relevant solvent shell on the photochemical behavior. Additionally, studies on the dimer of 7H4MC as well as its mono- and dihydrate are illustrated.

MO 10.15 Tue 16:30 Spree-Palais

Hidden charge states in soft xray laser produced nanoplasmas revealed by fluorescence spectroscopy — ●A. PRZYSTAWIK¹, L. SCHRÖDTER¹, M. MÜLLER², A. KICKERMANN¹, S. TOLEIKIS¹, M. ADOLPH², L. FLÜCKINGER², T. GHORKOVER², L. NÖSEL², M. KRIVONOVA², T. OELZE², Y. OVCHARENKO², D. RUPP², M. SAUPPE², D. WOLTER², S. SCHORB³, C. BOSTEDT³, T. MÖLLER², and T. LAARMANN¹ — ¹DESY Hamburg, Germany — ²TU Berlin, Germany — ³SLAC, Stanford, USA

Highly charged ions are formed in the center of composite clusters by strong free-electron laser pulses and they emit fluorescence on a femtosecond time scale before competing recombination leads to neutralization of the nanoplasma core. In contrast to mass spectrometry that detects remnants of the interaction, fluorescence in the extreme ultraviolet spectral range provides fingerprints of transient states of high energy density matter. Spectra from clusters consisting of a xenon core and a surrounding argon shell show that a small fraction of the fluorescence signal comes from multiply charged xenon ions in the cluster core. Initially, these ions are as highly charged as the ions in the outer shells of pure xenon clusters with charge states up to at least 11+.

MO 10.16 Tue 16:30 Spree-Palais

Gas Phase Vibrational Spectroscopy of Messenger-tagged Aluminum Oxide Clusters Anions — ●MATIAS R. FAGIANI¹, XI-AOWEI SONG¹, WIELAND SCHÖLLKOPF¹, SANDY GEWINNER¹, FLORIAN A. BISCHOFF², JOACHIM SAUER², and KNUT R. ASMIS^{1,3} — ¹Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany — ²Humboldt-Universität zu Berlin, Institut für Chemie, Brook-Taylor-Str. 2, D-12489 Berlin, Germany — ³Wilhelm-

Ostwald-Institut, Universität Leipzig, Linnéstr. 2, D-04103 Leipzig, Germany

Alumina structures of reduced dimensionality are of interest in astrophysics and atmospheric chemistry, as well as in nanostructured ceramic materials and solid catalysts. Little is known, experimentally, concerning the geometric structure of such clusters. Vibrational spectroscopy combined with electronic structure calculations provides more detailed insight into the geometric and electronic structure of these clusters.

Here, we present infrared photodissociation (IRPD) spectra of aluminum oxide cluster anions, focusing mainly on the fully-oxidized, electronic closed-shell clusters. The cluster anions are formed in a sputtering source. Mass-selected anions are trapped, cooled to cryogenic temperatures and messenger-tagged (D_2) in a buffer gas filled ion trap. Photodissociation spectra are measured from 400 to 1200 cm^{-1} with the widely tunable IR radiation of the free electron laser FHI FEL. The spectra are assigned and cluster structures are determined by comparison with the results of density functional calculations.

MO 10.17 Tue 16:30 Spree-Palais

New Setup for Core-Level PES on free mass selected Metal Clusters — ●MICHAEL KÖTHER¹, PATRICE OELSSNER¹, JENS BAHN¹, VOLKMAR SENZ², CHRISTIAN BRAUN³, STEFFEN PALUTKE⁴, BERND VON ISSENDORFF⁵, ECKHART RÜHL⁶, GERD GANTEFÖR³, DIETER BAUER¹, JOSEF TIGGESBÄUMKER¹, and KARL-HEINZ MEIWES-BROER¹ — ¹Inst. für Physik Universität Rostock — ²Inst. für Biomed. Technik Universität Rostock — ³FB Physik Universität Konstanz — ⁴Inst. für Physik Universität Hamburg — ⁵Fak. für Physik Universität Freiburg — ⁶Physik und theoretische Chemie FU Berlin

Previous experiments at the FEL (FLASH) in Hamburg have shown distinct changes in the binding energy of core level electrons with respect to the cluster sizes. With higher photon energies available it is now possible to excite even deeper core electrons. On the other hand higher target densities are necessary to do qualitative research. We want to introduce a new setup for Core-Level PES utilizing a helium cooled RF-Trap for maximum target density and energy resolution.

The project is part of the Collaborative Research Center (SFB) 652.

MO 10.18 Tue 16:30 Spree-Palais

A Relativistic Time-Dependent Density Functional study of the excited states for the mercury dimer. — ●OSSAMA KULLIE — Institute for Physics, Department for Mathematics and Natural Science, Uni Kassel. And Institute de Quantique Chimie, Uni Strasbourg, France.

In this work [1] I present a time-dependent density functional (TDDFT) study for the ground-state as well as the excited states corresponding to the $(6s^2 + 6s6p)$, $(6s^2 + 6s7s)$ and $(6s^2 + 6s7p)$ atomic asymptotes for the mercury dimer Hg₂. We analyze its spectrum obtained from all-electron calculations performed with the relativistic Dirac-Coulomb and relativistic spinfree Hamiltonian as implemented in Dirac-Package. Our result is excellent for the most of the lower excited states and very encouraging for the higher excited states, it shows generally good agreements with experimental results and outperforms other theoretical results. This enables us to give a detailed analysis of the spectrum of Hg₂ especially for the relativistic effects, the spin-orbit interaction, and the performance of CAMB3LYP functional approximation and is enlightened for similar systems. [1] submitted to the J. chem. phys. 2013.

MO 10.19 Tue 16:30 Spree-Palais

Multiple time scale population transfer-dynamics in coupled electronic states — MARTIN KESS, CHRISTOPH BRÜNING, and ●VOLKER ENGEL — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Emil-Fischer-Str. 42, 97074 Würzburg, Germany

We regard the wave-packet dynamics in two electronic states which interact via a constant coupling element. Performing numerical calculations it is found that the time-dependent populations exhibit oscillatory variations with two characteristic periods. Whereas, as expected, one period is determined by the vibrational motion, it is shown that Rabi-type oscillations occur which are influenced by the parameters of the potential energy curves, the coupling and the amplitudes in the two states on one hand, and by the nuclear motion on the other. An analysis of the numerical results is performed within various levels of approximation.

Furthermore, we investigate how these structures survive if the one-

dimensional model is extended to more degrees of freedom.

MO 10.20 Tue 16:30 Spree-Palais

Carrier Envelope Phase Effects induced by weak multicycle pulses: localized quantum dynamics in double well potentials — ●KILIAN HADER^{1,2}, KLAUS RENZIEHAUSEN^{1,2}, and VOLKER ENGEL^{1,2} — ¹Institut für Physikalische und Theoretische Chemie, Uni Würzburg — ²Campus Nord, Am Hubland, Emil-Fischer-Str. 42, 97074 Würzburg, Germany

We study the laser-driven quantum dynamics in a double well potential. Within a two-pulse excitation scheme the first pulse prepares a linear combination of excited states with ungerade symmetry. The interaction with a second uncorrelated pulse of low intensity results in coherent superpositions of states with gerade and ungerade symmetry. This is associated with a localization of excited state wave packets. It is shown that the carrier envelope phase of the second laser pulse critically influences this time-dependent localization.

MO 10.21 Tue 16:30 Spree-Palais

Stochastic wave-function approach to two-dimensional vibronic spectroscopy — ●JOHANNES WEHNER¹, MIRJAM FALGE¹, WALTER T. STRUNZ², and VOLKER ENGEL¹ — ¹Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Emil-Fischer-Str. 42, 97074 Würzburg, Germany — ²Institut für Theoretische Physik, TU Dresden, 01062 Dresden, Germany

Wave-packet dynamics derived from the time-dependent Schrödinger equation is nicely illustrative because it appeals to our classical intuition. However, there is no single reduced wave-packet for a system interacting with an environment. Nevertheless, the wave packet picture for the system dynamics can still be used under certain assumptions concerning the system-bath coupling. If the reduced density matrix fulfills a master equation of the Lindblad type, stochastic wave function equations can be set up which, in the average, are equivalent to the Lindblad master equation. We apply the quantum-diffusion stochastic approach to two-dimensional vibronic spectroscopy. Spectra are calculated and related to the underlying stochastic wave-packet dynamics.

MO 10.22 Tue 16:30 Spree-Palais

The time-scale of nonlinear events driven by strong fields: Can one control the spin-coupling before ionization runs over? — ●MIRJAM FALGE¹, PATRICIA VINDEL-ZANDBERGEN², VOLKER ENGEL¹, MANFRED LEIN³, BO Y. CHANG⁴, and IGNACIO R. SOLA² — ¹Universität Würzburg, Institut für Physikalische und Theoretische Chemie, Campus Nord, Emil-Fischer-Str. 42, 97074 Würzburg, Germany — ²Departamento de Química Física, Universidad Complutense, 28040 Madrid, Spain — ³Leibniz Universität Hannover, Institut für Theoretische Physik, Appelstraße 2, 30167 Hannover — ⁴School of Chemistry (BK21), Seoul National University, Seoul 151-747, Republic of Korea

An initially populated spin manifold interacting with an external field can decay via spin-coupling or via ionization. Using a simple two-level Hamiltonian we investigate the relation between spin coupling and ionization rate and identify conditions for an efficient spin-control by suppressing ionization. The results are confirmed in solving the time-dependent Schrödinger equation for the interaction of a laser field with a spin-coupled model system where two electrons and a nucleus move in a collinear configuration. It is thus shown, that quantum control of intersystem crossing can indeed be effective if the intensity of the external field and the accompanying Stark-shift is adjusted properly to the spin coupling-strength.

MO 10.23 Tue 16:30 Spree-Palais

Laser-Driven Wave Packet Dynamics of Metal-Dicarbonyls — ●MATEUSZ LISAJ and OLIVER KÜHN — Institute of Physics, University of Rostock, Rostock, Germany

Metal-carbonyls play important roles in physiological and catalytic processes. In this contribution we aim at obtaining fundamental insight into the interactions responsible for bond dissociation by applying shaped laser pulses to steer molecular quantum dynamics. Specifically, $CpCo(CO)_2$ is studied on the basis of a four-dimensional reactive potential energy surfaces, containing the two carbonyl vibrations as well as the respective metal-carbonyl bond dissociation coordinates. Potential end dipole moment surfaces are obtained using density functional theory with the B3LYP functional and the LanL2DZ basis set. The time-dependent Schrödinger equation is solved employing the multi-configuration time-dependent Hartree method. Laser pulse optimiza-

tion is performed with the goal to transfer as much energy as possible from the initially excited carbonyl vibration onto the metal-carbonyl bond such as to trigger bond breaking.

MO 10.24 Tue 16:30 Spree-Palais

Photoelectron Circular Dichroism of Chiral Molecules from Multiphoton Ionization with Femtosecond Laser Pulses: Intensity and Ellipticity studies — CHRISTIAN LUX¹, STEFANIE ZÜLLIGHOVEN¹, CRISTIAN SARPE¹, 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

Photoelectron Circular Dichroism (PECD) - i.e. the difference of the Photoelectron Angular Distribution (PAD) from ionization with left circularly polarized light and the PAD from ionization with right circularly polarized light - 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. From the results on variation of the laser intensity, we conclude an underlying dissociative ionization. The PECD can be unambiguously attributed to direct ionization of the parent ion. Ellipticity studies show the robustness of the PECD effect. [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)

MO 10.25 Tue 16:30 Spree-Palais

Twin Mass Peak Ion Source for Determination of Chiral Enantiomers with Femtosecond Laser Pulses — CHRISTIAN LUX¹, TOM RING¹, STEFANIE ZÜLLIGHOVEN¹, JENS KÖHLER¹, CRISTIAN SARPE¹, 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

In the recent past, a specific anisotropy was observed in the gas phase ionization of chiral enantiomers using circularly polarized laser pulses [1,2]. The implementation of a twin mass peak ion source enabled the direct determination of this anisotropy applying nanosecond laser pulses [1]: A focused circularly polarized laser beam passes a second lens, is back-reflected via a mirror and with changed helicity again focussed into the time-of-flight mass spectrometer. A small spatial displacement of both foci results in time-separated mass spectra. Fluctuations in the shot-to-shot laser pulse energy, the gas density or the ion detection can be circumvented. However, this technique is not suitable for femtosecond laser pulses which are strongly affected by optical dispersion. In this contribution we discuss the current status of an in-line optical setup applicable for femtosecond laser pulses. [1] C. Logé, U. Boesl, Chem. Phys. Chem. **12**, 1940-1947 (2011)

[2] P. Horsch, G. Urbasch, K.-M. Weitzel, Chirality **24**, 684-690 (2012)

MO 10.26 Tue 16:30 Spree-Palais

PEGASUS: Building an intense spin-polarized electron gun - status report — MICHAEL LESTINSKY¹, DANIEL SCHURY¹, SIEGBERT HAGMANN¹, CHRISTOPHOR KOZHUHAROV¹, and THOMAS STÖHLKER^{1,2} — ¹GSF Helmholtzzentrum für Schwerionenforschung, D-64291 Darmstadt — ²Helmholtzinstitut Jena, Friedrich-Schiller-

Universität Jena, D-07743 Jena.

The PEGASUS project aims at building an intense and portable spin-polarized electron gun for experiments in crossed beams arrangements at various ion beam facilities. The electron beam will cover energies between 1 and 10 keV at electron currents up to 100 μ A. As source material we will utilize laser-induced electron emission from GaAs photocathodes which will be prepared in a state of negative electron affinity. With a set of electrostatic lenses and benders, the electrons will be transported to the interaction zone and Wien-filters will be used for controlling the spin orientation.

We give a status report on our progress for building the setup and discuss foreseen experiments.

MO 10.27 Tue 16:30 Spree-Palais

Direkte Bestimmung der stereochemischen Absolutkonfiguration mittels Coulomb-Explosion-Imaging — MARTIN PITZER¹, KRISTINA ZERBE¹, MAKSIM KUNITSKI¹, ALLAN S. JOHNSON¹, TILL JAHNKE¹, HENDRIK SANN¹, FELIX STURM¹, LOTHAR PH. H. SCHMIDT¹, HORST SCHMIDT-BÖCKING¹, REINHARD DÖRNER¹, JÜRGEN STÖHNER², JULIA KIEDROWSKI³, MICHAEL REGGELIN³, SEBASTIAN MARQUARDT³, ALEXANDER SCHIESSER³, ROBERT BERGER³ und MARKUS S. SCHÖFFLER¹ — ¹Institut für Kernphysik, Goethe-Universität Frankfurt am Main — ²Zürcher Hochschule für Angewandte Wissenschaften, Zürich, Schweiz — ³Clemens-Schöpf-Institut, TU Darmstadt

Die Untersuchung molekularer Chiralität ist von weitreichendem Interesse in der Chemie und Biologie, aber auch für fundamentale Fragen wie die Paritätsverletzung. Trotz zahlreicher experimenteller Ansätze ist die Bestimmung der absoluten Konfiguration, d.h. der mikroskopischen Händigkeit, nach wie vor für viele flüssige und gasförmige Substanzen nur indirekt möglich. Wir zeigen unsere kürzlich veröffentlichten Ergebnisse [1], in denen es gelungen ist, die absolute Konfiguration der chiralen Methanderivate CHBrClF und CHBr³⁵Cl³⁷Cl mittels Coulomb Explosion Imaging (CEI) zu bestimmen. Mithilfe der Cold Target Recoil Ion Momentum Spectroscopy (COLTRIMS) war es möglich, für individuelle Moleküle die Händigkeit zu ermitteln. Diese Strukturinformation kann nun mit Photo-Elektron-Spektren kombiniert werden, um so ein detaillierteres Verständnis des Photo-Elektronen-Dichroismus (PECD) zu erhalten.

[1] M.Pitzer et al., Science Vol. 341, p.1096 (2013)

MO 10.28 Tue 16:30 Spree-Palais

Chiralitätsbestimmung einfacher organischer Moleküle mittels Coulomb Explosion Imaging — KRISTINA ZERBE, MARTIN PITZER, MAKSIM KUNITSKI, LOTHAR PH. H. SCHMIDT, GREGOR KASTIRKE, MARKUS S. SCHÖFFLER, HORST SCHMIDT-BÖCKING und REINHARD DÖRNER — Institut für Kernphysik, Goethe-Universität Frankfurt am Main

Chiralität ist eine wichtige Eigenschaft von Molekülen, die in Physik, Chemie und Biochemie von großer Bedeutung ist. Die Bestimmung der absoluten Konfiguration, also der räumlichen Anordnung der Atome oder Atomgruppen um ein chirales Zentrum, ist bislang nur für kristallisierbare Stoffe mittels anomaler Röntgenbeugung möglich.

Unsere Gruppe [1] hat mittels Coulomb Explosion Imaging (CEI) und Cold Target Recoil Ion Moment Spectroscopy (COLTRIMS) bereits die absolute Konfiguration von Brom-Chlor-Fluormethan und weiteren Methanderivaten bestimmen können. Aufbauend darauf soll dies nun für größere gasförmige Moleküle (mehr als ein Kohlenstoffatom) erweitert werden. Die nun folgenden Untersuchungen des Fragmentierungsverhaltens von 2-Hydroxypropansäure und 2-Brompropansäure in Abhängigkeit von der Laserintensität, -pulslänge und -polarisation sollen vorgestellt werden.

[1] M. Pitzer et al., Science Vol. 341, p.1096 (2013)

MO 11: Biomolecules 1

Time: Wednesday 14:00–15:45

Location: BEBEL HS213

MO 11.1 Wed 14:00 BEBEL HS213

Probing Protonation Sites of Isolated Flavin Molecules via IR Spectroscopy — ALAN GÜNTHER¹, JUDITH LANGER¹, GIEL BERDEN², JOS OOMENS³, and OTTO DOPFER¹ — ¹Institut für Optik und Atomare Physik, Hardenbergstr. 36, 10623 Berlin, Germany — ²Radboud University Nijmegen, Institute for Molecules and Materials, FELIX facility, Toernooiveld 7, 6525 ED Nijmegen — ³University of

Amsterdam, Science Park 904, 1098XH Amsterdam, The Netherlands
Infrared spectra of the isolated protonated flavin molecules lumichrome, lumiflavin, riboflavin (vitamin B2), and the biologically important cofactor of blue-light receptors flavin mononucleotide are measured in the fingerprint range (600-1850 cm^{-1}) by means of IR multiple photon dissociation (IRMPD) spectroscopy. Using density functional theory calculations, the geometries, relative energies, and

linear IR absorption spectra of several low energy isomers have been calculated. Comparison of the calculated IR spectra with the measured IRMPD spectra reveals that the N10 substituent at the isoalloxazine ring influences the protonation site of the flavin. Lumichrome with a hydrogen substituent is only stable as N1 hydrogenated tautomer and protonates at N5 of the pyrazine ring. The presence of the sugar unit in riboflavin leads to protonation at N1 of the pyrimidinedione moiety, and methyl substitution in lumiflavin stabilizes the tautomer which is protonated at O2. In contrast, flavin mononucleotide occurs as both the O2 and N1 protonated tautomers. The frequencies and relative intensities of the two C=O stretch vibrations in protonated flavins serve as reliable indicators for their protonation site.

MO 11.2 Wed 14:15 BEBEL HS213

Rotational Spectrum of 4-Aminobenzonitrile - Nuclear Quadrupole Coupling Constants of Two Chemically Distinct Nitrogen Atoms — •THOMAS BETZ^{1,2,3}, SABRINA ZINA^{1,2,3}, JACK B. GRANEEK^{1,3}, and MELANIE SCHNELL^{1,2,3} — ¹Max Planck Institute for the Structure and Dynamics of Matter, Luruper Chaussee 149, D-22761 Hamburg — ²The Hamburg Centre for Ultrafast Imaging, Luruper Chaussee 149, D-22761 Hamburg — ³Center for Free-Electron Laser Science, Notkestrasse 85, D-22607 Hamburg

4-aminobenzonitrile belongs to the class of para-substituted benzonitriles, which evoked attention because some representatives display double-fluorescence effects. In 4-aminobenzonitrile this has not been observed and this study aims to improve the understanding of the underlying principles.

The rotational spectrum between 2 and 8.5 GHz of this molecule in the gas phase is reported. Due to the two chemically distinct nitrogen atoms the observed transitions show a complex hyperfine structure. From the determination of the nuclear quadrupole coupling constants, information on the electronic environment of these atoms could be inferred. The results are compared to related molecules and indicate a reason for the absence of double-fluorescence effects in 4-aminobenzonitrile.

MO 11.3 Wed 14:30 BEBEL HS213

Histidine-cation interaction and microsolvation from first principles — •MARKUS SCHNEIDER¹, VOLKER BLUM^{1,2}, CARSTEN BALDAUF¹, and MATTHIAS SCHEFFLER¹ — ¹Fritz-Haber-Institut der MPG, Berlin, Germany — ²MEMS, Duke University, Durham, U.S.A.

Protein-cation interactions play a crucial role in shaping the three-dimensional structure of protein. Of special importance here is the histidine side chain that is, among other examples, involved in the metal cation complexation by the Alzheimer A β peptide. Our work aims for understanding the binding of cations by histidine as well as its effect on the peptide structure from first principles. However, the first critical point is the appropriateness of the chosen level of theory for quantitative predictions of such interactions. To that end, we focus on the effect of microsolvation, with either Zn²⁺ or a H₂O molecule or both in competition, on the protonation state of the His sidechain. We first assemble a large ensemble of possible conformations from empirical force field calculations. Then, we use these conformations to benchmark the performance of density-functional theory based methods against high-level coupled-cluster calculations. In particular, we assess the PBE generalized gradient approximation as well as the PBEh and B3LYP hybrid density functionals, all of them corrected for long-range dispersion with either the pairwise Tkatchenko-Scheffler scheme or a newly developed many-body dispersion scheme (MBD*).

MO 11.4 Wed 14:45 BEBEL HS213

Elucidating the Building and Breaking of Hydrogen Bonds: Two color delay dependent IR probing of torsional isomerization — •JOHANNES LANG, MAXIMILIAN GAFFGA, FABIAN MENGES, KEVIN MULLER, WERNER THIEL, and GEREON NIEDNER-SCHATTEBURG — Technische Universität Kaiserslautern, Germany

Infrared multiple-photon dissociation (IR-MPD) spectroscopy can be used to characterize organometallic complexes in the gas phase [1]. Here, we investigate a flexible arrangement of a single Ag(I) center with two suitable ligands via IR MPD spectroscopy and density functional theory (DFT) based calculations. Bands of at least two isomers can be assigned in the experimental spectrum. These bands correspond to NH—O or CH—O stabilized rotational conformers, in which the Ag(I) ion serves as a pivot. Delay dependent two color IR-MPD measurements elucidate changes of the relative isomer population. We characterize rotational barriers, the change of vibrational frequencies and IR intensities along the isomerization pathway by DFT based cal-

culations [2].

References:

- [1] Nosenko, Y., et al., Physical Chemistry Chemical Physics, 2013. 15(21): p. 8171-8178.
- [2] Gaffga, M., Lang, J.I., Menges, F., Muller, K., Thiel, W., Niedner-Schatteburg, G., manuscript in preparation. 2014.

MO 11.5 Wed 15:00 BEBEL HS213

Femtosecond 2D-IR spectroscopy of SCN - a vibrational probe for protein dynamics — •DANIELA KERN-MICHLER, LUUK VAN WILDEREN, HENRIKE M. MÜLLER-WERKMEISTER, and JENS BRE-DENBECK — Institut für Biophysik, Gothe Universität / Frankfurt am Main

Novel vibrational probes like nitrile, azide or thiocyanate (SCN) groups [1] are useful to obtain dynamic and site-specific information in proteins. We measured steady-state and time-resolved infrared (IR) spectra of methylthiocyanate (MeSCN) in various solvents with different polarities and H-bonding character to characterize the SCN moiety as an infrared label. To demonstrate the applicability in a protein, we introduced a S¹³C¹⁵N group into bovine hemoglobin (Hb) [2]. The central SCN stretch frequency depends on the solvent properties, making SCN a suitable probe for its local environment. In addition, we measured time-resolved two-dimensional infrared (2D-IR) spectra of S¹³C¹⁵N in Hb, which hint at local structural rearrangements on an ultrafast timescale. The low central frequency observed in the protein compared to MeSCN indicates that the label is not hydrogen bonded, although we measure a shorter vibrational lifetime (T₁) than for MeSCN. The rich molecular detail the label provides on its local surroundings, combined with its relatively long T₁ (34 ps), makes the SCN vibration thus a promising IR label to resolve protein dynamics.

[1] Lindquist et al. (2009) PCCP, 11 (37), 8105-8380 [2] Fafarman et al. (2006). JACS, 128, 13356-13357 [3] Kim et al. (2013) Chem. Rev. 113 (8), pp 5817-5847

MO 11.6 Wed 15:15 BEBEL HS213

Ultrafast pump-probe spectroscopy on the initial photoreaction of bathy-phytochrome Agp2 of *Agrobacterium tumefaciens* reveals transient protonation processes — •PATRICK SINGER¹, SYBILLE WÖRNER², TILMAN LAMPARTER², and ROLF DILLER¹ — ¹Dept. of Physics, Univ. Kaiserslautern, 67663 Germany — ²Dept. of General Botany, KIT, 76131 Germany

Plant photomorphogenesis is regulated by the photoreceptor phytochrome, a light controlled protein in plants, bacteria and fungi. Photoinduced interconversion between a thermally stable red absorbing state Pr and the biologically active far red absorbing state Pfr is initiated by light absorption of the open chain tetrapyrrole bilin chromophore, undergoing a rapid isomerization reaction (femtosecond timescale)¹. In this study we investigate Agp2 from *A. tumefaciens*, which fundamentally differs from common phytochromes in its photodynamic properties caused by a thermally (in-)stable (Pr)Pfr ground state (bathy-phytochrome). Previous investigations reveal protonation/deprotonation of the Pr chromophore with an unusually low pKa = 7.85 (pKa > 11 in common phytochromes)². We performed transient UV/Vis pump-probe spectroscopy on the fs-time scale in different buffer-conditions (H₂O/D₂O; pH6 - pH9) to investigate spectral and kinetic properties of the primary photoreaction of the Pr state. Transient measurements reveal two fast decaying intermediate species dependent on buffer condition. The results are discussed in context of chromophore protonation processes. ¹C. Schumann et al. Biophys.J. 94 3189-3197(2008) ²B. Zienicke et al. JBC 288 31738-31751(2013)

MO 11.7 Wed 15:30 BEBEL HS213

Ultrafast Spectroscopic Studies of Cyclic Tetrazolium Cell Dyes and their Photoproducts — •FLORIAN KANAL, DOMENIK SCHLEIER, NINA SCHOPF, and PATRICK NUERNBERGER — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

Tetrazolium salts are cyclic dyes which are commonly used for testing cell viabilities by detecting formazans as their enzymatically metabolised ring-open forms. The influence of light is often ignored in these assays, although for some tetrazolium salts photochemical reduction to formazans has been reported.

The ultrafast photochemistry of two of the most prominent tetrazolium salts, 2,3,5-Triphenyl-tetrazolium chloride (TTC) and 3-(4,5-Dimethyl-2-thiazolyl)-2,5-diphenyl-tetrazolium bromide (MTT) was investigated in alcoholic and different pH-valued aqueous solutions by ultrafast spectroscopy. Both compounds yield the formazan via re-

action channels involving different short-living ring-open and -closed structures within few nanoseconds either in alcoholic (TTC) or in basic (MTT) solution.

Depending on the solvent, TTC-formazan shows either the formation of a bicyclic radical or huge conformational changes in the formazan

skeleton upon long-time irradiation. In contrast, the ultrafast dynamics of TTC- and MTT-formazan are almost unaltered if the solvent is changed. As only the primary steps of both reactions take place on an ultrafast time-scale, involvement of a long-living state is most likely for the final product formation.

MO 12: Experimental Techniques 2

Time: Wednesday 14:00–15:30

Location: BEBEL SR144

Invited Talk MO 12.1 Wed 14:00 BEBEL SR144
Ultrafast X-ray Auger Probing of photoexcited molecular dynamics — B. K. MCFARLAND¹, J. FARRELL^{1,2}, S. MIYABE¹, F. TARANTELLI³, A. AGUILAR⁴, N. BERRAH⁵, C. BOSTEDT⁶, J. D. BOZEK⁶, P. H. BUCKSBAUM^{1,2}, J. C. CASTAGNA⁶, R. N. COFFEE⁶, J. P. CRYAN^{1,2}, L. FANG⁵, R. FEIFEL⁷, K. J. GAFFNEY¹, J. M. GLOWNIA^{1,2}, T. J. MARTINEZ^{1,8}, M. MUCKE⁷, B. MURPHY⁵, A. NATAN¹, T. OSIPOV⁵, V. S. PETROVIC^{1,2}, S. SCHORB⁶, TH. SCHULTZ⁹, L. S. SPECTOR^{1,2}, M. SWIGGERS⁶, I. TENNEY^{1,2}, S. WANG^{1,2}, J. L. WHITE^{1,2}, W. WHITE⁶, and M. GUEHR^{1,2} — ¹PULSE, SLAC, Menlo Park, USA — ²Physics/Applied Physics, Stanford Univ., Stanford, USA — ³Chemistry, Univ. Perugia, and ISTM-CNR, Perugia, Italy — ⁴ALS, LBNL, Berkeley, USA — ⁵Physics, WMU., Kalamazoo, USA — ⁶LCLS, SLAC Menlo Park, USA — ⁷Physics/Astronomy, Uppsala Univ., Uppsala, Sweden — ⁸Chemistry, Stanford Univ., Stanford, USA — ⁹Max-Born-Institut, Berlin, Germany

Molecules efficiently and selectively convert light energy into other energy forms through ultrafast nuclear and electronic rearrangements. Efforts to distinguish the role of nuclear and electronic dynamics remain challenging. We performed femtosecond ultraviolet pump - x-ray Auger probe spectroscopy at the linac coherent light source (LCLS). This method can be used to separate electronic and nuclear relaxation in photoexcited molecular dynamics and we address the UV photo-protection mechanism of isolated nucleobases. We find a very fast electronic relaxation within 200 fs after excitation, which cannot be described within the Born-Oppenheimer approximation.

MO 12.2 Wed 14:30 BEBEL SR144
X-ray diffraction from aligned gas-phase molecules with a free-electron laser — STEPHAN STERN^{1,2}, JOCHEN KÜPPER^{1,2}, HENRY N. CHAPMAN^{1,2}, and DANIEL ROLLES¹ — ¹Center for Free-Electron Laser Science (CFEL), DESY, Hamburg, Germany — ²University of Hamburg, Hamburg, Germany

We report experimental results on x-ray diffraction of state-selected and aligned ensembles of the prototypical molecule 2,5-diodobenzonitrile using the Linac Coherent Light Source. The results confirm necessary steps toward x-ray diffractive imaging of such weakly-scattering molecular samples: the ability to provide quantum-state selected ensembles of molecules, to strongly laser-align these, and to perform single-photon detection with the photon detector, even above severe background levels. The approach is suitable for studying ultrafast dynamics of small isolated molecules utilizing the femtosecond x-ray pulses from XFELs together with femtosecond pulses from optical lasers in future pump-probe experiments.

This work was carried within a collaboration, for which J. Küpper, H. Chapman and D. Rolles are spokespersons. The collaboration consists of CFEL (DESY, MPG, University Hamburg), Fritz-Haber-Institute Berlin, MPI Nuclear Physics Heidelberg, MPG Semiconductor Lab, Aarhus University, FOM AMOLF Amsterdam, Lund University, MPI Medical Research Heidelberg, TU Berlin, Max Born Institute Berlin, and SLAC Menlo Park, USA. The experiments were carried out using CAMP (designed and built by the MPG-ASG at CFEL) at the LCLS (operated by Stanford University on behalf of the US DOE.)

MO 12.3 Wed 14:45 BEBEL SR144
Nuclear magnetic resonance spectroscopy on a (5nm)³ sample volume — TOBIAS STAUDACHER¹, CARLOS MERILES², FRIEDEMANN REINHARD¹, and JÖRG WRACHTRUP¹ — ¹Universität Stuttgart and Research Center SCoPE, Stuttgart, Germany — ²The City College of New York, CUNY New York, USA

We have recently demonstrated nuclear magnetic resonance spectroscopy (NMR) on a nanoscale volume ((5nm)³) of various liquid and solid samples, a size comparable to a single macromolecule [1,2].

Access to such small length scales is enabled by an atomically small magnetic field sensor, the nitrogen-vacancy center in diamond. This color defect can be employed as a magnetic sensor by performing precision spectroscopy on its spin sublevels.

I will discuss the details of this experiment as well as one future prospect, hyperpolarization of the sample. It seems feasible to increase magnetization of the sample volume to a level close to unity by coherently transferring magnetization from the optically polarized NV center to the sample.

[1] T. Staudacher et al., *Science* **339**, 561 (2013)

[2] H.J. Mamin et al., *Science* **339**, 557 (2013)

MO 12.4 Wed 15:00 BEBEL SR144
Femtosecond time-resolved photoelectron spectroscopy with XUV pulses in aqueous solution utilizing the liquid microjet technique — JAN METJE^{1,2}, MARIO BORGFWARDT^{1,2}, ALEXANDRE MOGUILJEVSKI^{1,2}, ALEXANDER KOTHE^{1,2}, NICHOLAS ENGEL^{1,2}, MARTIN WILKE^{1,2}, RUBA AL-OBAYDI^{1,2}, DANIEL TOLKSDORF^{1,2}, ALEXANDER FIRSOV³, MARIA BRZHEZINSKAYA³, ALEXEI ERKO³, IGOR KIYAN^{1,2}, and EMAD FLEAR AZIZ^{1,2} — ¹Joint Ultrafast Dynamics Lab in Solutions and at Interfaces (JULiq), Helmholtz-Zentrum Berlin, Albert-Einstein-Str. 15, 12489 Berlin — ²Freie Universität Berlin, FB Physik, Arnimallee 14, 14195 Berlin — ³Institute for Nanometer Optics and Technology, Helmholtz-Zentrum Berlin, Albert-Einstein-Str. 15, 12489 Berlin

We present a newly built laser-based tabletop setup for time resolved photoelectron spectroscopy of liquids and dissolved molecules. The system provides femtosecond extreme ultraviolet (XUV) light generated as high harmonic (HHG) from a titanium sapphire laser as the probe. The spatial, spectral, and temporal characteristics of the XUV beam are presented. Monochromatization of the XUV light with minimum temporal pulse distortion is the central issue of this work. Off-center reflection zone plates are shown to be superior to gratings when selection of a desired harmonic is carried out with the use of a single optical element. A cross-correlation technique was applied to characterize the performance of the zone plates in the time domain. By using laser pulses of 25 fs length to pump the HHG process, a pulse duration of 45 fs for monochromatized harmonics was achieved.

MO 12.5 Wed 15:15 BEBEL SR144
Nuclear spin control with a transient electron spin ancilla — HELMUT FEDDER¹, SANG-YUN LEE¹, MATTHIAS WIDMANN¹, TORSTEN RENDLER¹, MARCUS DOHERTY², NEIL MANSON², and JÖRG WRACHTRUP¹ — ¹Physikalisches Institut und Research Center SCoPE, University Stuttgart, Germany — ²Laser Physics Center, Research School of Physics and Engineering, Australian National University, Canberra, Australia

Electron spins associated with point defects in crystals are promising systems for solid state quantum technology [1-3]. In particular, defects with a spin-less ground state and an excited triplet state have been proposed as universal ancillae for addressing nuclear spins [2]. In here we demonstrate the control of an individual ¹³C lattice nuclear spin in diamond by exploiting a novel electron spin defect that features an excited triplet state. Using optical and microwave control, we demonstrate coherent manipulation of the triplet electron spin and characterize its photo-physics. We then show coherent manipulation of the nuclear spin in the spin-less electronic ground state.

[1] J.J.L. Morton et al. Solid-state quantum memory using the 31P nuclear spin. *Nature* **455**, 1085 (2008).

[2] V. Filidou et al. Ultrafast entangling gates between nuclear spins using photoexcited triplet states. *Nature Phys.* **8**, 596 (2012).

[3] P.C. Maurer et al. Room-Temperature Quantum Bit Memory Exceeding One Second. *Science* **336**, 1283 (2012).

MO 13: Posters 3: Cold Molecules, Helium Nano Droplets, and Experimental Techniques

Time: Wednesday 16:30–18:30

Location: Spree-Palais

MO 13.1 Wed 16:30 Spree-Palais

Centrifuge deceleration of electrically guided continuous beams of polar molecules — ●THOMAS GANTNER, SOTIR CHERVENKOV, XING WU, JOSEF BAYERL, ANDREAS ROHLFES, MARTIN ZEPPENFELD, and GERHARD REMPE — Max-Planck-Institut für Quantenoptik, 85748 Garching, Germany

We present experimental results from a novel and versatile decelerator for continuous beams of neutral polar molecules [1]. A beam of polar molecules from an effusive nozzle is injected at the periphery of a rotating disk and electrically guided [2] to the centre along a spiral-shaped electrostatic quadrupole guide. Thus the molecules climb up the centrifugal potential hill and get decelerated as they propagate. The deceleration of continuous beams of neutral CF_3H , CH_3F , and CF_3CCH is demonstrated. The combination of the centrifuge decelerator with a cryogenic buffer-gas cooling source [3] is expected to result in the production of even larger fluxes of slow and moreover internally cold molecules amenable to further cooling [4].

[1] S. Chervenkov et al., Phys. Rev. Lett. (in press), arXiv:1311.7119 (2013)

[2] S.A. Rangwala et al., Phys. Rev. A 67, 043406 (2003)

[3] L.D. van Buuren et al., Phys. Rev. Lett. 102, 033001 (2009)

[4] M. Zeppenfeld et al., Nature 491, 570 (2012)

MO 13.2 Wed 16:30 Spree-Palais

Combining a continuous centrifuge decelerator with a cryogenic buffer-gas source — ●XING WU, SOTIR CHERVENKOV, THOMAS GANTNER, JOSEPH BAYERL, MARTIN ZEPPENFELD, and GERHARD REMPE — Max-Planck-Institut für Quantenoptik, Hans-Kopfermann-Str. 1, 85748 Garching, Germany

The production of large samples of slow molecules with high internal-state purity is still a major challenge in the fast-growing research field of cold molecules. We propose a promising solution by combining a recently demonstrated centrifuge decelerator [1] with a cryogenic buffer-gas source [2]. The centrifuge decelerator is based on the centrifugal potential in a rotating frame, enables a continuous deceleration of molecular beams to almost a standstill, and is applicable to a large range of species. The cryogenic source provides high intensities of internally cold molecules. In order to optimize the flux of the electrically guided beams [3], both the supersonic and the effusive regime of the buffer-gas cooling have been explored. The obtained results indicate that the optimum is achieved in the so-called boosted effusive regime. In combination with the centrifuge decelerator, continuous beams at intensities of several $10^9 \text{s}^{-1} \text{mm}^{-2}$ occupying a minimum number of internal states, and with close-to-zero velocities are conceivable.

[1] S. Chervenkov et al., Phys. Rev. Lett. (in press); arXiv:1311.7119

[2] L.D. van Buuren et al., Phys. Rev. Lett. 102, 033001 (2009)

[3] S.A. Rangwala et al., Phys. Rev. A 67, 043406 (2003)

MO 13.3 Wed 16:30 Spree-Palais

Finding pathways for creation of cold molecules by laser spectroscopy — ●IVO TEMELKOV, HORST KNÖCKEL, and EBERHARD TIEMANN — QUEST und Inst. f. Quantenoptik, Leibniz Universität Hannover

The diatomic alkali molecules are of serious interest for the cold matter physics. This research is focused on developing a model for efficient transfer of $^{23}\text{Na}^{39}\text{K}$ molecules from the $\text{Na}(3s)+\text{K}(4s)$ asymptote to the lowest levels of the singlet ground state. The experiment is done in an ultrasonic beam apparatus, using a Λ -scheme with fixed pump and scanning dump laser. The signals are observed as dark lines on a constant fluorescence. The intermediate level is strongly perturbed helping to overcome the singlet-triplet transfer prohibition. In the beam NaK is created in its singlet ground state and the transfer is driven to the triplet state, but this scheme can work also in the reversed direction. Precise potential energy curves for singlet and triplet ground state already exist from previous work of our group. We observe highly resolved hyperfine spectra of various rovibrational levels (from $v=2$ up to the asymptote, for $N=4,6,8$) of the $a^3\Sigma^+$ state with resolution better than 10MHz. Two different theoretical models are used in parallel to describe the observations. The first one is based on molecular parameters. The other uses potential curves, taking into account all couplings as functions of the internuclear distance and calculating the energy levels for all the quantum numbers in a coupled

state model. With these results an efficient pathway for the creation of cold NaK molecules is demonstrated.

MO 13.4 Wed 16:30 Spree-Palais

Development of a versatile ion trap based experimental station for the study of biomolecular ions — ●TIM MICHAELSEN, SUNIL KUMAR, THORSTEN BEST, and ROLAND WESTER — Institut f. Ionenphysik und Angewandte Physik, Universität Innsbruck

Intramolecular vibrational relaxation of biomolecules upon UV excitation is the key process determining their stability against radiation damage[1]. However, the details of the mechanism behind this process are still poorly understood.

We are currently developing a versatile ion trap based experimental station which will allow us to examine this process in detail. The biomolecular ions are produced in an electrospray ion source[2] with an ion-funnel interface[3], which has already been implemented and characterized. The ions are then guided by a linear quadrupole and mass selected by a second quadrupole. They will be stored and cooled down to 4K in a unique 16-pole ion trap, which is designed to allow for laser irradiation of ions normal to the trap axis similar to our wire-based octupole ion trap[4]. The ions extracted from the ion trap are then analyzed using a reflectron-based time-of-flight mass spectrometer. To investigate the details of the intermolecular vibrational relaxation of chromophore-based molecules, we will choose the fluorescent protein chromophore anion as a model system.

[1] A.V. Bochenkova, L.H. Andersen, Faraday Discuss.163, 297-319 (2013); [2] Gaskell, S. J., J. Mass Spectrom. 32, 677-688. (1997); [3] Ryan T Kelly, et al., Mass Spectrom. Rev., 29, 294-312 (2010); [4] J. Deiglmayr, et al., Phys. Rev. A 86, 043438 (2012);

MO 13.5 Wed 16:30 Spree-Palais

Spatial separation of molecular clusters and conformers — ●THOMAS KIERSPEL^{1,2}, DANIEL A. HORKE¹, YUAN-PIN CHANG¹, 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

Many complex molecules exhibit multiple structural isomers (conformers) [1], even at the low temperatures in a cold molecular beam [2]. These conformers, as well as molecular clusters, typically differ in their electric dipole moment. The dispersion of a molecular beam using the electric deflector can be exploited for the spatial separation of the different species present in the beam [3]. We present the spatial separation of both, *cis*- and *trans*-, conformers of 3-fluorophenol (3FP) [4], the separation of indole-water dimers from a cluster soup [5], and discuss the prospects for conformer separation of glycine, the smallest amino acid. 3FP is a prototypically large molecule and conformational clean samples enable novel experiments like laser pump-, and ultrafast X-ray or photoelectron diffraction probe, to image conformer-interconversion processes. Molecular clusters like indole-water are bridging the gap between isolated and solvated molecules and are a key to understand the molecule-solvent interaction and the influence of the environment on the molecular function.

[1] Suenram et al., J. Mol. Spectrosc. 72, 372-382 (1978) [2] Rizzo et al., J. Chem. Phys. 83, 4819 (1985) [3] Chang et al., Science 342, 98-101 (2013) [4] Kierspel et al., Chem. Phys. Lett. 591, 130-132 (2014) [5] Trippel et al., Phys. Rev. A 86, 033202 (2012)

MO 13.6 Wed 16:30 Spree-Palais

Supersonic molecular beams for high-precision measurements using a traveling-wave decelerator — ●SREEKANTH CHIRAYATH MATHAVAN, JOOST E VAN DEN BERG, CORINE MEINEMA, JANKO NAUTA, RONNIE HOEKSTRA, LEO HUISMAN, IMKO SMID, and STEVEN HOEKSTRA — university of groningen, groningen, the netherlands

We are building an experimental setup to perform high-precision experiments to test fundamental physics with cold molecules. We combine supersonic expansion with traveling-wave deceleration and laser cooling to create dense, translationally and internally cold molecular samples in the same quantum state. We started our experiments with the SrF molecule, which we already showed can be decelerated, and is laser coolable, which enhances its sensitivity towards high-precision experiments. On this poster, we present our work on the creation of an intense supersonic beam of SrF .

MO 13.7 Wed 16:30 Spree-Palais

Rotational-dynamics studies of state-selected molecules — ●JENS S. KIENITZ^{1,2}, SEBASTIAN TRIPPEL¹, TERENCE G. MULLINS¹, NELE L. M. MÜLLER¹, and JOCHEN KÜPPER^{1,2,3} — ¹Center for Free-Electron Laser Science, DESY — ²Center for Ultrafast Imaging, University of Hamburg — ³Department of Physics, University of Hamburg

State-selected, strongly aligned and oriented molecular ensembles serve as ideal samples to image ultrafast chemistry in the molecular frame, for instance, through molecular-frame photo-electron angular distributions or electron- or x-ray diffraction. We developed advanced techniques to manipulate the motion of molecules in cold supersonic beams at a kHz repetition rate [1]. State-, conformer-, and size-selection of neutral molecules was achieved through the dispersion of the molecular beam in the electric deflector. The state-selected molecules were laser aligned or mixed-field oriented in laser and static electric fields. We demonstrated strong alignment as well as mixed-field orientation for different molecular samples up to a 1 kHz repetition rate. We investigated the effects of widely varying pulse laser durations (50 fs to 500 ps), reaching from the impulsive regime to the adiabatic regime, which allowed us to disentangle previous experimental approaches. So far unobserved details of the intricate rotational dynamics were observed in the intermediate regime, e.g., for laser pulses on the order of the rotational period of the molecules.

[1] S.Trippe et al., Mol. Phys., 111, 1738 (2013)

MO 13.8 Wed 16:30 Spree-Palais

Deceleration and deflection of cold Hydrogen molecules by a Rydberg Stark decelerator — ●JOHANNES DEIGLMAYR, PITT ALLMENDINGER, JOSEPH AGNER, and FRÉDÉRIC MERKT — ETH Zurich, Laboratory of Physical Chemistry, Zurich, Switzerland

In the past years our group developed a miniature decelerator for atoms and molecules in Rydberg-Stark-states [1]. It consists of a two-dimensional array of electrodes on a printed circuit board which creates weak electric fields with large field gradients, making the deceleration of atoms and molecules in Rydberg states with high n possible.

Recently we have realized a bent version of our decelerator which deflects the decelerated beam by 10° from the axis of supersonic expansion. The deflected samples of atoms and molecules have translational temperatures on the order of 100mK, which makes them ideally suited for trapping or collision experiments. We will present these results and the current status of the experiment.

[1] S. D. Hogan et al., PRL 108, 063008 (2012); P. Allmendinger et al., PRA 88, 043433 (2013)

MO 13.9 Wed 16:30 Spree-Palais

Perspectives for translational temperature diagnostics of trapped ions by evaporative losses. — ●OLGA LAKHMANSKAYA¹, THORSTEN BEST¹, SUNIL KUMAR¹, ERIC ENDRES¹, DANIEL HAUSER¹, RICO OTTO², STEPHANIE EISENBACH³, ALEXANDER VON ZASTROW⁴, and ROLAND WESTER¹ — ¹Universität Innsbruck, A-6020, Innsbruck, Austria — ²University of California, San Diego, California 92093-0332, United States — ³Physikalisches Institut, Albert-Ludwigs-Universität Freiburg, 79104 Freiburg, Germany — ⁴Institute for Molecules and Materials IMM, Radboud University Nijmegen, 6525 AJ Nijmegen, The Netherlands

We present a scheme for translational temperature diagnostics of ions in a 22-pole ion trap using data for OH⁻ and D⁻ anions. This scheme is based on the strong dependence of the lifetime of the ions on temperature. While examining loss rates as a function of buffer gas temperature we have found a breakdown of thermalisation for trap temperatures lower than 25 K. We have investigated this feature in more detail and have found that it does not depend on either buffer gas or the trapping parameters. We have also investigated two regimes for ion losses, either over one of the two end cap electrodes (axial direction) or over the effective potential (radial direction). We have found that evaporation over the end caps may be suitable for translational thermometry.

MO 13.10 Wed 16:30 Spree-Palais

Quantum simulations with trapped molecules with microwave field — ●YUBING YANG — Department of Physics, University of Freiburg, Stefan-Meier-Strasse 19, D-79104 Freiburg, Germany

Ultracold quantum gases offer a unique setting for quantum simulation of interacting many-body systems. Systems of trapped molecules can be accurately controlled and manipulated with microwave field, a large variety of interactions can be engineered with high precision

and measurements of relevant observables can be obtained with nearly 80% efficiency. Here, the authors discuss prospects for quantum simulations using systems of trapped molecules with microwave field, and review the available set of quantum operations and first proof-of-principle experiments for both analog and digital quantum simulations with trapped molecules with microwave field. Here we review recent advances in technology and discuss progress in a number of areas where experimental results have already been obtained.

MO 13.11 Wed 16:30 Spree-Palais

Laser cooling of heavy diatomic molecules — ●CORINE MEINEMA, JOOST VAN DEN BERG, SREEKANTH MATHAVAN, JANKO NAUTA, LORENZ WILLMANN, KLAUS JUNGMANN, and STEVEN HOEKSTRA — Rijksuniversiteit Groningen, Groningen, the Netherlands

We will combine our travelling-wave decelerator with laser cooling to obtain a gas of ultra cold polar molecules, all in the same quantum state. After deceleration the gas of SrF molecules has a temperature of 150 mK. Laser cooling will be used to reduce this to 150 μ K. Due to the complex rotational and vibrational structure, laser cooling is for most types of molecules not possible. However, SrF has an almost closed rovibrational transition, that we can use to scatter sufficient photons before the molecule will be pumped into a dark state. We will present our experimental approach and the latest results.

MO 13.12 Wed 16:30 Spree-Palais

MEASUREMENT OF THE LIFETIME OF THE FIRST VIBRATIONALLY EXCITED STATE OF MGH+ — ●OSCAR O. VERSOLATO^{1,4}, MARIA SCHWARZ^{1,4}, ANDERS K. HANSEN², ALEX D. GINGELL², ALEXANDER WINDBERGER¹, LUKASZ KŁOSOWSKI³, JOACHIM ULLRICH⁴, FRANK JENSEN², JOSÉ R. CRESPO LÓPEZ-URRUTIA¹, and MICHAEL DREWSEN² — ¹Max-Planck-Institut für Kernphysik, Heidelberg, Germany — ²Aarhus University, Denmark — ³Nicolaus Copernicus University, Torun, Poland — ⁴Physikalisch-Technische Bundesanstalt, Braunschweig, Germany

Diatomic hydrides are a basic class of molecules with dipole-allowed rovibrational transitions, readily observable in the interstellar medium (ISM) both in their neutral and singly ionized states. In general, their abundances in the ISM are derived from mm-wave and deep infrared absorption and emission lines for which precise knowledge of the relevant rovibrational transition strengths is required. We present here a method for obtaining such transition strengths employing a direct laser excitation scheme and exploiting the cryogenic environment of our cryogenic Paul trap CryPTEX, in which blackbody radiation induced rotational dynamics are slowed down and excellent vacuum conditions exist, enabling the measurement of the lifetime of the first vibrationally excited state in MgH⁺ by means of laser excitation to this state, followed by resonance enhanced two-photon dissociation of the ions that were sympathetically cooling into a Coulomb crystal. The method presented here can readily be extended to other molecules of particular astrophysical relevance.

MO 13.13 Wed 16:30 Spree-Palais

ULTRA-TENUOUS ROTATIONAL BUFFER GAS COOLING OF COULOMB-CRYSTALIZED MGH+ — ANDERS K. HANSEN¹, ●OSCAR O. VERSOLATO^{2,3}, LUKASZ KŁOSOWSKI⁴, SIMON B. KRISTENSEN¹, ALEX D. GINGELL¹, MARIA SCHWARZ^{2,3}, ALEXANDER WINDBERGER², JOACHIM ULLRICH³, JOSÉ R. CRESPO LÓPEZ-URRUTIA², and MICHAEL DREWSEN¹ — ¹QUANTOP, Department of Physics and Astronomy, Aarhus University, Denmark — ²Max-Planck-Institut für Kernphysik, Heidelberg, Germany — ³Physikalisch-Technische Bundesanstalt, Braunschweig, Germany — ⁴Nicolaus Copernicus University, Torun, Poland

The preparation of cold molecules is of particular interest for studies of cold chemistry, astrophysics, as well as for fundamental physics. Recent progress in direct laser cooling methods has shown great promise, but these methods are extremely molecule-specific. Buffer gas cooling in multipole traps, although universally applicable, also has significant drawbacks because of the high densities required. Here, we present for the first time results of tenuous helium buffer gas cooling of the rotational degrees of freedom of MgH⁺ molecular ions at 4-5 orders of magnitude lower pressure than in typical buffer gas settings. The MgH⁺ ions were sympathetically laser cooled into a Coulomb crystal after which very efficient buffer gas cooling was performed, reaching a record-low molecular ion internal temperature. Effective tuning of the temperature between 7 and 60K, by changing micromotion amplitudes, was demonstrated. Tenuous buffer gas cooling should also enable studies on cold single, heavy molecules of biological interest.

MO 13.14 Wed 16:30 Spree-Palais

Detecting the Rotational State of Electrically Trapped Polyatomic Molecules — ●ROSA GLÖCKNER, ALEXANDER PREHN, MARTIN ZEPPEFELD, and GERHARD REMPE — Max-Planck-Institut für Quantenoptik, Hans-Kopfermann-Str. 1, 85748 Garching

The determination of the internal state of molecules is a key element for their precise control. However, especially for polyatomic molecules, state sensitive detection can be a considerable challenge due to predissociation and fragmentation when addressing electronic transitions with uv light. We present here an alternative for trapped molecules using depletion.

Our method is based on the difference of signals with and without depletion: driving transitions from selected rotational states to untrapped states. Therefore, the detection of the molecule itself can be state independent and thus a simple method like a quadrupole mass spectrometer (QMS) is sufficient. We demonstrate two variations of the method, infrared depletion and microwave depletion, and discuss the assets and drawbacks.

In addition to rotational J-levels, we can address individual M-sublevels. Using this we can extract the narrow field distribution in our homogeneous-field electric trap[1] by measuring the Stark-broadened line shape of the transition between the $|J = 3, K = 3, M = 3\rangle \rightarrow |J = 4, K = 3, M = 4\rangle$ states of CH_3F . 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).

MO 13.15 Wed 16:30 Spree-Palais

Sympathetic cooling of OH^- ions using Rb atoms in a MOT — ●HENRY LOPEZ¹, BASTIAN HÖLTKEMEIER¹, JULIAN GLÄSSEL¹, PASCAL WECKESSER¹, ERIC ENDRES², THORSTEN BEST², ROLAND WESTER², and MATTHIAS WEIDEMÜLLER¹ — ¹Physikalisches Institut, Ruprecht-Karls-Universität Heidelberg, Deutschland — ²Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck, Österreich

Molecular ions are usually caught in high-order multipole radio frequency traps and cooled sympathetically by He buffer gas. In order to reach lower temperatures for a wider range of molecular ions we investigate replacing He with laser-cooled atoms. In particular, we use a new hybrid ion-atom trap to study the interaction of ultracold Rb atoms with mass-selected OH^- -water clusters. While the Rb atoms are stored in a Dark-SPOT trap loaded from a 2D-MOT, the ions are trapped in an octupole radio frequency trap consisting of thin wires, enabling optical access to the trapping region. For efficient cooling a dense cloud of atoms is needed, preferably in the ground state to avoid inelastic collisions. In our setup we trap up to 4×10^8 atoms at peak densities of up to 3×10^{11} atoms/cm³ with almost all atoms being in the absolute ground state. For these parameters our numerical simulations suggest that cooling the ions by at least one order of magnitude can be achieved. On this poster I report on the status of our experiment, its limitations and possible applications.

MO 13.16 Wed 16:30 Spree-Palais

Stretching the Envelope in Crossed Beam Experiments — ●ALEXANDER VON ZASTROW, JOLIIN ONVLEE, SJOERD VOGELS, DAVID H. PARKER, and SEBASTIAAN Y. T. VAN DE MEERAKKER — Radboud University Nijmegen, Institute for Materials and Molecules, Heyendaalseweg 135, 6525AJ Nijmegen

The fundamental understanding of intermolecular interactions is essential for various fields, such as astrophysics. Highly detailed information about these interactions can be extracted from atomic and molecular collisions in crossed beam experiments.

Combining the Stark deceleration technique with velocity map imaging results in high resolution experiments which give detailed information about intermolecular interactions. This is shown in the observation of diffraction oscillations in the differential cross section of state-to-state inelastic scattering of NO molecules with rare gas atoms. Further advantage of this high resolution will be taken in the future. In particular, our approach is ideally suited to investigate low-energy quantum scattering resonances with unprecedented accuracy. The measurement of such phenomena can make a significant contribution to a better understanding of intermolecular interactions, both experimentally and theoretically.

MO 13.17 Wed 16:30 Spree-Palais

Observation of coherent interference and determination of strengths and signs of an electric- and magnetic-dipole tran-

sition moment in OH — ●H.C. SCHEWE¹, D. ZHANG¹, X. WANG¹, G. MEIJER^{1,2}, B. SARTAKOV³, R. W. FIELD⁴, and N. VANHAECKE^{1,5} — ¹Fritz-Haber-Institut der Max-Planck-Gesellschaft Faradayweg 4-6, 14159 Berlin — ²Radboud University Nijmegen, Institute for Molecules and Materials, Heijendaalseweg 135, 6525 AJ Nijmegen, the Netherlands. — ³General Physics Institute RAS, Vavilov Street 38, 119991 Moscow, Russia — ⁴Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139 — ⁵Laboratoire Aimé Cotton, CNRS, Université Paris-Sud, 91405

Spectroscopic investigations of particles are a fundamental method to investigate its structure and dynamics. Higher order transitions like a magnetic-dipole or electric-quadrupole transition reveal a deeper insight into the quantum system itself. Usually these transitions are many orders of magnitude weaker and, therefore, experimentally challenging to determine.

The magnetic dipole transition in the OH radical has been determined in two different ways: (1) using a static electric field, whereby an electric-dipole transition moment is admixed to a magnetic-dipole transition, and (2) using the method of Stark interference: by applying a static magnetic and static electric field, a coherent interference of the electric- and magnetic transition dipole moment could be observed, and the strength and the sign of the transition momenta was determined.

MO 13.18 Wed 16:30 Spree-Palais

En route to many-body physics with ^{23}Na - ^{40}K ground-state polar molecules — ●ZHENKAI LU, NIKOLAUS BUCHHEIM, TOBIAS SCHNEIDER, IMMANUEL BLOCH, and CHRISTOPH GOHLE — Max-Planck-Institut für Quantenoptik, Hans-Kopfermann-Straße 1, 85748 Garching, Germany

Ultra cold quantum gases with long-range dipolar interaction promise exciting new possibilities for quantum simulation of strongly interacting many-body systems.

New classes of many-body phases (like super solids and stripe phases) are on the horizon and ferroelectric phases of highly polarizable systems are expected [1][2].

We have constructed an experimental apparatus aiming to create ultracold chemical stable ground-state ^{23}Na - ^{40}K molecules. We will present the design considerations, implementation and performance of the experiment. In addition, we will present our recent results on producing ^{23}Na - ^{40}K Feshbach molecules.

[1] G. Pupillo, *et al.* Condensed Matter Physics with Cold Polar Molecules. arXiv: 0805.1896 (2008).

[2] M. Iskin, *et al.* Ultracold Heteronuclear Molecules and Ferroelectric Superfluids. *Phys. Rev. Lett.* **99**, 110402 (2007).

MO 13.19 Wed 16:30 Spree-Palais

Imaging photoionization dynamics of doped Helium Nanodroplets and molecular Rydberg states — ●JOHANNES VON VANGEROW¹, ALEXANDR BOGOMOLOV², BARBARA GRÜNER¹, ALEXEY BAKLANOV², FRANK STIENKEMEIER¹, and MARCEL MUDRICH¹ — ¹Physikalisches Institut, Universität Freiburg, Hermann-Herderstr. 3, 79108 Freiburg, Germany — ²Institute of Chemical Kinetics and Combustion, Institutskaya Str. 3, Novosibirsk 630090, Russia

With temperatures in the cold regime (0.38 K) and only weak interaction, doped Helium Nanodroplets are interesting environments to study perturbations of atoms and molecules induced by many particle interaction. Within this context, we will present results concerning the desorption dynamics of the heavy alkali atoms Rb and Cs from helium droplets. Both dopants are weakly attached to the droplet surface. By resonance enhanced multiphoton-ionization via low lying pseudo-diatom Σ - and Π -states and subsequent ion and electron imaging, we observe dissociation dynamics similar to that of a diatomic molecule and an energy transfer to the droplet during the desorption process, suggesting substantial He-droplet excitation.

The second part of the poster focuses on high-lying *gerade* Rydberg states of molecular iodine within the $[^2\Pi_{1/2}]_c8s; 0g$ and $[^2\Pi_{1/2}]_c8s; 1g$ band. In a collaborative^{1,2} velocity map imaging study, five different dissociation channels have been observed. One channel indicates predissociation via an ion pair state, the others correspond to predissociation via lower lying covalent Rydberg states.

MO 13.20 Wed 16:30 Spree-Palais

IR and UV spectroscopy of biomolecular ions in liquid helium droplets — ●DOO-SIK AHN, ANA ISABEL GONZALEZ FLOREZ, and GERT VON HELDEN — Fritz-Haber-Institut, Berlin, Germany

Liquid helium droplets are ideal nano-cryostats for the investigation of molecules because of intrinsic characters of superfluid helium droplets such as isothermality at 0.38 K, the weak interaction between the helium matrix and dopant, and a transparency over a wide spectral range from the far IR to the deep UV. For the application of this technique to the cooling and spectroscopic investigation of biomolecular ions in the gas phase, we have developed an experimental setup where mass/charge selected biomolecular ions picked up by helium droplets. The size-distributions of ion-doped He droplets are analyzed by the measurement of arrival time distributions at different acceleration field. IR and UV Spectroscopy can be performed by irradiating the ion-doped He droplets with a pulsed laser and monitoring ejected ions as a function of wavelength. We will report very recent result of IR spectroscopy of various peptide ions doped in He droplets using FHI(Fritz-Haber-Institut) free electron laser, and UV spectroscopy as well.

MO 13.21 Wed 16:30 Spree-Palais

LIF spectroscopy of laser-ablated atoms in He nanodroplets and dense He gas — ●SHARAREH IZADNIA, AARON LAFORGE, and FRANK STIENKEMEIER — Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str.3, 79104 Freiburg, Germany

Van der Waals forces make extremely weak intermolecular bonds and play a crucial role in physical, chemical, and biological systems. Until recently, helium dimers, with an average interatomic nuclear distance of 52 Å, were the weakest bound experimentally observed system [1]. Now, however, an even weaker system, LiHe dimers, has been found by Tariq et al.[2]. Using laser ablation of lithium in a cryogenically-cooled helium buffer gas, LiHe dimers were formed via a three body recombination process and experimentally observed by laser induced fluorescence (LIF)[2]. In our lab, we have recently developed a method to dope helium nanodroplets using a similar laser ablation setup. Surprisingly, it was found that not only were the ablated materials doped to nanodroplets, but they were also seeded in a cold He gas jet. In light of this and the previous work, we plan to perform LIF spectroscopy on laser ablated alkali atoms doped to nanodroplets and seeded in a dense gas. Our experimental approach along with the first results will be shown.

[1] R. E. Grisenti, W. Schöllkopf, J. P. Toennies, G. C. Hegerfeldt, T. Köhler, and M. Stoll, *Phys. Rev. Lett.* 85, 2284 (2000)

[2] N. Tariq, N. Al Taisan, V. Singh, and J. D. Weinstein, *Phys. Rev. Lett.* 110, 153201 (2013)

MO 13.22 Wed 16:30 Spree-Palais

Mass-resolved pump-probe spectroscopy of alkali-doped He nanodroplets — ●OLIVER JOHN¹, JOHANNES VON VANGEROW¹, HARALD SCHMIDT¹, DANIEL REICH², WOJCIECH SKOMOROWSKI², CHRISTIANE KOCH², FRANK STIENKEMEIER¹, and MARCEL MUDRICH¹ — ¹Physikalisches Institut, Universität Freiburg, Hermann-Herderstr. 3, 79108 Freiburg, Germany — ²Physikalisches Institut, Universität Kassel, Heinrich-Plettstr. 40, 34132 Kassel, Germany

Cold helium nanodroplets (400mK) possess several remarkable properties such as suprafluidity, making them attractive matrices for spectroscopy of a wide range of embedded atoms and molecules.

The first topic of this poster concerns Rb-doped He nanodroplets. The aim of this ongoing investigation is to understand the desorption dynamics of Rb dopants upon excitation and ionization by mass-resolved femtosecond pump probe spectroscopy via the pseudodiatomic $6p\Sigma$ and $6p\Pi$ states. Recent results show a pronounced drop of the ion yield for pump probe delays below one picosecond, suggesting either submersion of Rb ions or a reduced ionization cross section in the vicinity of He droplets.

The second topic focuses on vibrational wave packet dynamics within the A-state of lithiumiodide in the gas phase. From the pump-probe transients we derive properties of the potentials including coupling parameters at avoided curve-crossings by comparing to quantum dynamics simulations. In LiI doped He droplets we observe very fast relaxation dynamics, indicating strong interaction with the He.

MO 13.23 Wed 16:30 Spree-Palais

Allyl Radicals in Helium Nanodroplets — ●DANIEL LEICHT, DANIEL HABIG, GERHARD SCHWAAB, and MARTINA HAVENITH — Physical Chemistry 2, Ruhr-University Bochum, Germany

The allyl radical is the simplest π -conjugated hydrocarbon radical having an open-shell electronic structure due to its unpaired electron [1]. It has been firmly established that the allyl radical exhibits C_{2v} symmetry with a $2A_2$ ground electronic state [2]. Like all other C_3 -

hydrocarbon units allyl radicals are believed to be precursors in the formation of soot and polynuclear aromatic hydrocarbons [3]. Furthermore, the allyl radical is a key intermediate in tropospheric chemistry.

Superfluid helium nanodroplets have been demonstrated to be an effective tool for studying transient species such as radicals. Because of their high reactivity the knowledge of these systems and their interactions is still in its infancy. However, spectroscopy in helium nanodroplets makes it possible to investigate not only the bare allyl radical, but also its reactions and interactions with other molecules (e.g. O_2 or HCl) at 0.37 K.

[1] K. Tonokura and M. Koshi, *J. Phys. Chem. A* 2000, 104, 8456-8461

[2] J.Han et. al., *J. Chem. Phys.*, Vol. 116, No. 15, 15 April 2002

[3] T. Schultz and I. Fischer, *J. Chem. Phys.*, Vol. 109, No. 14, 8 October 1998

MO 13.24 Wed 16:30 Spree-Palais

NC₄₁₁₁ NTf₂ in Helium Nanodroplets — ●MATIN KAUFMANN, KENNY HANKE, TEEMU SALMI, GERHARD SCHWAAB, and MARTINA HAVENITH — Physikalisches Chemie II, Ruhr-Universität Bochum, Germany

Room temperature ionic liquids (ILs) are organic salts with a melting point around room temperature. Combinations of different cations and anions lead to a plethora of ILs and therefore provide room for many applications as in cleaning processes, gas storage and batteries. Due to their ionic nature, ILs possess a low vapor pressure, and there exist only few studies on gas phase spectroscopy.

Superfluid helium nanodroplets provide a soft matrix for the infrared spectroscopy of single molecules and small clusters. Vapor pressures of only 10^{-6} mbar are sufficient to incorporate molecules into the droplets. Through evaporative cooling the embedded molecules are then cooled to a temperature of 0.37 K where molecular motion is minimal, yielding clean spectra.

We hereby present IR spectra of buthyltrimethylammonium bis(trifluoromethylsulfon)imide (NC₄₁₁₁ NTf₂). By analyzing the vibrational bands for complexes with different numbers of ions, we obtain information on the interaction of the ions.

MO 13.25 Wed 16:30 Spree-Palais

Single-particle orbit tracking: A versatile tool for monitoring confined diffusion in nanoporous materials — ●DOMINIC RAITHEL¹, DANIEL ZALAMI¹, DOMINIQUE ERNST¹, UWE GERKEN¹, JÜRGEN KÖHLER¹, and MARKUS RETSCH² — ¹Lehrstuhl für Experimentalphysik IV Universität Bayreuth, 95447 Bayreuth, Deutschland — ²Lehrstuhl für Physikalisches Chemie I Universität Bayreuth, 95447 Bayreuth, Deutschland

Diffusion and transport processes play an important role in many fields of natural and material sciences. An example is confined diffusion in nanoporous materials, as they are used in catalytic converters. Diffusion processes were generally studied with fluorescence-correlation spectroscopy (FCS) as well as single-particle tracking (SPT) methods using high sensitive CCD or CMOS cameras. We demonstrate a versatile SPT-technique, lately proposed by J. Enderlein [1], called single-particle orbit tracking (SPOT). With SPOT a single fluorescent particle is traced with the rotating focus of the excitation laser orbiting the particle. SPOT allows to follow a fluorescent polymer bead for several minutes with a temporal resolution of 4 ms and a position accuracy in the range of 10 nm [2]. With SPOT we are able to reconstruct the restricted trajectory of a fluorescent polymer bead within an inverse opal nanostructure, a 3-dimensional porous silica structure with cavities in the range of 100 nm. Due to the high spatial accuracy of the SPOT technique we can map the topology of the sample.

[1] J. Enderlein, *Appl. Phys. B* (71), 773-777 (2000) [2] D. Ernst et al., *JOSA* (29), 1277-1287 (2012)

MO 13.26 Wed 16:30 Spree-Palais

Fast, precise, and widely tunable frequency control of a cw optical parametric oscillator — ●ALEXANDER PREHN, ROSA GLÖCKNER, MARTIN ZEPPEFELD, and GERHARD REMPE — Max-Planck-Institut für Quantenoptik, Hans-Kopfermann-Str. 1, 85748 Garching, Germany

Frequency combs offer a variety of new possibilities for frequency measurement and control. Here we report on the widely tunable, fast and precise frequency control of a commercially available optical parametric oscillator (OPO) locked to a frequency comb. In addition to stabilization to sub-MHz precision, the approach allows for fast frequency ramps in the whole tuning range of 100 GHz. Frequency ramps over

more than 10 GHz performed in less than 10 ms are demonstrated, with the OPO instantly relocked to the frequency comb after the ramp at any desired frequency.

We show two complementary examples for the application of the technique. First, rovibrational transitions of CFH₃ molecules stored in an electric trap [1] can be driven quasi-simultaneously even though the frequencies are spaced more than 10 GHz apart. Second, we show the frequency resolution of the system by means of Doppler-free spectra of rovibrational lines of H₂CO.

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

MO 13.27 Wed 16:30 Spree-Palais

Laser-induced acoustic desorption setup for the soft vaporization of large molecules — WILHELM F. FRISCH^{1,3}, 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

Laser-induced acoustic desorption (LIAD) is a promising technique for the preparation of dense plumes of intact neutral large molecules. Coupled with ionization and spectroscopic characterization techniques, it is shown to be of great utility for the analysis of a variety of thermally labile analytes.

We present our newly set up laser-induced acoustic desorption (LIAD) source, which is coupled to a time-of-flight (TOF) mass spectrometer (MS). In the LIAD experiment the molecules are deposited onto a thin (~10 μm) metal foil that is irradiated from the backside by the third harmonic of a Nd:YAG laser (355 nm). The induced shockwave travels through the foil and desorbs the molecules from the frontside of the foil [1]. The gas-phase molecules are subsequently strong-field ionized by a 40 fs Ti:Sapphire laser (800 nm) and mass-selectively detected in a TOF-MS. We discuss the efficiency of the source as well as the detailed characteristics of the created gas-phase sample as a function of experimental parameters, such as laser pulse energy and duration or foil parameters.

[1] B. Linder *et al.*, *Anal. Chem.* **57**, 895 (1985)

MO 13.28 Wed 16:30 Spree-Palais

Characterization of a 6 K Ring-Electrode Ion-Trap used for IR Photodissociation Experiments in a Triple Mass Spectrometer — TIM ESSER¹, NADJA HEINE¹, and KNUT R. ASMIS^{1,2} — ¹Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin, Germany — ²Wilhelm-Ostwald-Institut für Physikalische und Theoretische Chemie, Universität Leipzig, Linnéstrasse 2, D-04103 Leipzig, Germany

Mass-selective infrared photodissociation (IR-PD) spectroscopy combined with electronic structure calculations, is currently one of the most generally applicable techniques to determine the structure of gas phase cluster ions. To assure that the clusters are in their vibrational ground state they are typically buffer-gas cooled in a cryogenic ion trap. Here, we focus on the characterization of a linear ring-electrode radio-frequency (rf) ion-trap used in a 6K ion trap triple mass spectrometer. Preliminary results on the partially rotationally-resolved IR-PD spectrum of the singly hydrated ammonium ion, NH₄⁺(H₂O), allow to determine the rotational temperature as a function of the rf amplitude, buffer-gas pressure and store time. Apart from thermalization, the trap allows for bunching of the continuous ion beam and the attachment of messenger atoms or molecules. A genetic algorithm was developed, in order to automatically optimize the three sets of voltages, which are applied to the 12 pairs of ring electrodes during filling, storing and extraction. We further discuss the influence of the form of the trapping potential as well as the length of the store time on the size, shape and rotational temperature distribution of the ion packages.

MO 13.29 Wed 16:30 Spree-Palais

Development of an in-situ electrochemical flowcell for soft x-ray absorption and emission spectroscopy — CHRISTOPH SCHWANKE and KATHRIN AZIZ-LANGE — Helmholtz-Zentrum Berlin für Materialien und Energie, BESSY GmbH, Albert-Einstein-Strasse 15, 12489 Berlin, Germany

The investigation of liquid-solid interfaces with soft x-ray absorption and emission spectroscopy is interesting for dye sensitized solar cells, fuel cells, batteries, water splitting, corrosion and electrodeposition. Adding electrodes to a flowcell gives the possibility to get electronic structure information and the oxidation state of these systems in-situ, meaning while a voltage is applied. Additional to the information

gained with x-ray absorption and emission spectroscopy the system can be evaluated with cyclic voltammetry in our three electrode setup. Future experiments will investigate a fully working dye sensitized solar cell based on a Zn-porphyrin dye (YD2-O-C8) and a cobalt polypyridine redox couple. The investigations will cover the interactions between the components of dye sensitized solar cells. In this poster we will present details of this experimental technique and first results of cyclic voltammetry.

MO 13.30 Wed 16:30 Spree-Palais

An optical pipeline for femtosecond diffractive imaging — RICK KIRIAN¹, SALAH AWEL^{1,2,3}, NIKO ECKERSKORN⁴, ANDREI RODE⁴, JOCHEN KÜPPER^{1,2,3}, and HENRY CHAPMAN^{1,2,3} — ¹Center for Free-Electron Laser Science, DESY, Hamburg — ²Center for Ultrafast Imaging, University of Hamburg — ³Department of Physics — ⁴Australian National University, Canberra, Australia

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 emerging new paradigms. It consists of directing a stream of randomly oriented protein microcrystals or molecules across the focus of the XFEL beam. However, delivering single molecules to a sub-micron x-ray focus remains a considerable challenge. Current sample delivery efficiencies for single-molecule 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. Our experiments are presently aimed at transversely confining streams of particles as they exit an aerosol injector, which produces a 50 μm diameter stream, with a counter-propagating “hollow” quasi-Bessel beam. The experiment exploits radiation pressure and/or thermal forces arising from the interaction of the particles with surrounding gas [1].

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

MO 13.31 Wed 16:30 Spree-Palais

Dynamics of a nano-electromechanical rotor driven by single-electron tunneling — ALAN CELESTINO, PABLO CARLOS LÓPEZ VÁZQUEZ, and ALEXANDER EISEL — MPIPES, Dresden, Germany

We discuss a nano-electromechanical rotor driven by single-electron tunneling. A possible realization could be a nanotube with quantum dots attached on its extremities, which can freely rotate about a double-walled nanotube axis. The system is driven using a bias voltage between source and drain contacts. Using a few relevant parameters one can set the rotor's dynamics to either intermittent oscillations/rotations or continuous rotational motion. The connection between the dynamical regimes and the current through the device is established. The effect of tuning initial conditions is also addressed, showing a bistable behaviour in the system's phase space. Among the possible applications of such device stand out the signal amplification, current rectification and viscosity measurements.

[1] A. Croy and A. Eisel, *EPL (Europhys Lett)* **98**, 68004

MO 13.32 Wed 16:30 Spree-Palais

Vibronic line-shapes of polymeric cis-Indolenine squaraine dyes — CHRISTOPH BRÜNING¹, EILEEN WELZ¹, SEBASTIAN F. VÖLKER², CHRISTOPH LAMBERT², and VOLKER ENGEL¹ — ¹Universität Würzburg, Institut für Physikalische und Theoretische Chemie, Emil-Fischer-Str. 42, 97074 Würzburg — ²Universität Würzburg, Institut für Organische Chemie, Am Hubland, 97074 Würzburg

Using a vibronic coupling model we analyze measured absorption and emission spectra of cyclic polymeric cis-Indolenine squaraine dyes. From theory, features in the absorption spectra are identified as vibronic structures. The trimer exhibits unusual emission properties which can be explained taking at least two intra-monomer vibrational modes and a geometry distortion disturbing the symmetry into account.

MO 13.33 Wed 16:30 Spree-Palais

Discrimination between new and aged ETFE plastic samples using Raman spectroscopy and chemometric analysis — ALEXANDRU POPA, RASHA HASSANEIN, ANAIS COLIBABA, and ARNULF MATERNY — Jacobs University Bremen, Bremen, Germany

Ethylene-tetra-fluoro-ethylene (ETFE) a fluorine based plastic has

gained widespread popularity due to its unique properties. ETFE is assumed to be stable against solar degradation, acid and alkali proof, and has a low friction coefficient, which enhances its resistance to atmospheric pollution such as dust or dirt particles. Beside these properties, ETFE is a lightweight transparent material and transmits all wavelengths of the solar spectrum. Therefore, it has been increasingly used in building applications. In our contribution, we present results of our recent work where we have applied Raman spectroscopy and chemometric analysis in order to study both 28 years old and new ETFE samples. The goal was to verify the predicted stability of the material. In this context excitation wavelengths of 514.5 and 785 nm have been used. The investigated ETFE samples were supplied by Vector Foiltec GmbH Bremen. The old samples had been partially in long-term use in roof structures and partially stored as reference samples in archives. Raman spectra of the investigated samples have been statistically treated using principal component analysis (PCA) analysis. A clear separation between the samples of different ages has been obtained for the Raman data obtained with 785 nm excitation. Raman spectra obtained with a 514.5 nm excitation only yielded a smaller separation into two clusters.

MO 13.34 Wed 16:30 Spree-Palais

Ultrafast Charge Migration Induced by Inner-Shell Vacancy in Diiodomethane — ●MAXIMILIAN HOLLSTEIN and DANIELA PFANKUCHE — Jungiusstraße 9, 20355 Hamburg

The ultrafast charge migration on the sub-femtosecond timescale following the inner-shell ionization of an iodine atom of the diiodomethane molecule is investigated theoretically using a truncated configuration interaction method. A significant charge redistribution induced by the inner-shell ionized iodine atom was found which takes place during the first 100 as. Except for fluctuations, the observed charge redistribution remains stationary on the femtosecond timescale. The importance of two-electron correlations within the charge redistribution process is studied by consideration of two-particle correlation functions.

MO 13.35 Wed 16:30 Spree-Palais

Hierarchy of stochastic pure state wavefunctions for open quantum systems — DANIEL SÜSS¹, WALTER T. STRUNZ¹, and ●ALEXANDER EISEL² — ¹TU Dresden — ²MPI-PKS

A method is presented to efficiently solve open quantum system problems with a non-Markovian structured environment. The approach is based on the Non-Markovian quantum state diffusion (NMQSD). We derive a hierarchy of stochastic differential equations, which can be solved numerically efficient and which converges rapidly to the exact reduced density matrix. We demonstrate the usefulness of the method by considering the spin-boson problem, electronic excitation transfer in the light-harvesting Fenna-Matthews-Olson (FMO) complex and the calculation of absorption spectra of molecular aggregates.

MO 13.36 Wed 16:30 Spree-Palais

The nature of the chemical bond between Carbon and Fluorine in Perfluorocarbons — ●TIM BRANDENBURG¹, MARCUS AGÅKER³, KAAAN ATAK^{1,2}, MIKA PFLÜGER¹, KATHRIN AZIZ-LANGE¹, CHRISTOPH SCHWANKE¹, TRISTAN PETIT¹, JAN-ERIK RUBENSSON³, and EMAD FLEAR AZIZ^{1,2} — ¹Joint Ultrafast Dynamics Lab in Solutions and at Interfaces (JULiQ) Helmholtz-Zentrum Berlin für Materialien und Energie, Albert-Einstein-Strasse 15, 12489 Berlin, Germany — ²Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany — ³Department of Physics and Astronomy, Uppsala University, Box 516, SE 751 20 Uppsala, Sweden

Perfluorocarbons are a special family of molecules, which rarely exist in nature due to the high energy required to build the carbon-fluorine bond. The strong electronegative effect of fluorine on neighboring atoms is still awaiting a clear electronic structure picture description. The insight to be gained is proposed to be the origin of the unique functionalities of these systems. We have used soft X-ray XAS/XES/RIXS to draw a full electronic picture of the unoccupied and occupied molecular orbitals in solution. The effect of fluorine was observed and fingerprinted on Perfluorodecalin as a model system. The obtained experimental spectra are explained with ab initio calculations using ORCA.

MO 13.37 Wed 16:30 Spree-Palais

Fine structure and fragmentation of n=4 states in H₃ — ●STEFFEN J. MEYER, PEER C. FECHNER, and HANSPETER HELM — Albert-Ludwigs-Universität, Freiburg, Germany

Neutral triatomic hydrogen is the most simple polyatomic molecule, and a prototype of molecular degrees of freedom, of molecular interaction and of nonadiabatic couplings in particular.

In this contribution we present our results on the three-body fragmentation of principal quantum number n=4 states in H₃, which are coaxially or perpendicularly excited using a narrowband tunable diode laser in a keV neutral beam.

Precise continuous frequency tuning allows us to measure and compare the fine structure splitting of the vibrational ground state and vibrational excited states. The splitting depends on the coupling of electronic spin with the various angular momenta of the molecule.

The excited states decay primarily by predissociation into the continuum of three neutral H atoms. Time- and position-sensitive detectors allow to record in coincidence the three slow (≈ 1 eV) neutral ground state hydrogen atoms which emerge in predissociation.

Coincident detection of the three correlated atoms from a single molecule permits to reconstruct the centre-of-mass momentum vectors of the three hydrogen atoms. This experiment, when repeated for many molecules ($\approx 10^4$) delivers a map of momentum correlation of the three H atoms. The observed distribution is a measure of the phase-space dependent action of nonadiabatic coupling which allows the bound state to exit into the continuum.

MO 13.38 Wed 16:30 Spree-Palais

On the equivalence of spatial wave function and complete characterization of linear fragment momenta after many-body breakup — ●PEER C. FECHNER and HANSPETER HELM — Physikalisches Institut, Albert-Ludwigs-Universität Freiburg

At the example of triatomic hydrogen, we discuss the equivalence of the spatial and momentum wave functions of a many-body system as they evolve after a fragmentation process (Phys.Chem.Chem.Phys., 2014, 16, 453).

State selected H₃ molecules predissociate into the repulsive ground-state and undergo the 3-body decay $H_3 \rightarrow H(1s) + H(1s) + H(1s)$. The correlated fragment momentum vectors of the hydrogen atoms are recorded in the laboratory frame in triple coincidence. Prudent design of the experiment permits to trace out the nuclear frame alignment in the laboratory (the photofragment angular distribution) to arrive at correlated fragment momentum vectors in the center-of-mass. Accumulation of typically $\sim 10^4$ such observations yields a probability map of final momentum configurations, equivalent to the modulus square of the momentum wave function long after the decay. Comparison with the known initial spatial wave function suggests a close relationship of spatial and momentum wave function, which is predicted by theory in the form of the *imaging theorem*. We conclude that prudent imaging of many-body fragmentation provides a laboratory view of the squared many-body wave function at a spatial scale of molecular dimensions at which fragments exit into the realm of independent free particles.

MO 13.39 Wed 16:30 Spree-Palais

Molecular Frame Photoelectron Angular Distributions in Dissociating 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 elucidating time-resolved molecular dynamics. Indeed, one of the main driving forces behind the development of the FEL is the possibility to perform x-ray diffractive imaging in 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. The theory of photoelectron-molecule scattering has been studied thoroughly and a number of successful experiments relying on this concept have already been performed at synchrotrons with ground state molecules.

Here, we theoretically investigate the possibility to probe the dissociation dynamics of CF₃I molecules induced by excitation at 266 nm, using the photoelectrons generated by a time-delayed soft x-ray pulse. As a first step, the photoelectron angular distributions of a fixed in space CF₃I molecule in its ground state are calculated with the aid of the Schwinger variational principle and are compared to the predictions from an intuitive forward scattering model.

MO 13.40 Wed 16:30 Spree-Palais

Laser photothermal emission spectroscopy of gases — ●FELIX AXTMANN and JOHANNES HERBST — Fraunhofer IPM, Freiburg, Deutschland

Laser spectroscopy is a selective and sensitive tool for spectral analyzing molecules in the gas phase. Powerful quantum cascade lasers (QCL) enable the application of laser photothermal emission spectroscopy (LPTES). We demonstrate this for a stand off detection of a narrowband and broadband absorber in the gas phase. With LPTES the sample gas is heated up by the QCL using the vibrational rotational transition of the fundamental mode. Detection of the emit-

ted radiation can be performed either by broadband single detectors or infrared cameras. For analyzing the spectral emission we use a Fouriertransform-Infrared spectrometer (FTIR). By the excitation of a single rotational line in the v_4 vibrational mode of methane (1306 cm^{-1}) a complete vibrational spectrum is obtained. This research and measurement technique is used for the development of a methane leak detection system.

MO 14: Cold Molecules 2

Time: Thursday 10:30–12:30

Location: BEBEL HS213

MO 14.1 Thu 10:30 BEBEL HS213

Probing the orientation of $^{87}\text{Rb}_2$ molecules in the $a^3\Sigma_u^+$ rovibrational ground state by measuring the polarizability — ●MARKUS DEISS, BJÖRN DREWS, BENJAMIN DEISSLER, and JOHANNES HECKER DENSCHLAG — Institut für Quantenmaterie, Universität Ulm, Albert-Einstein-Allee 45, D-89081 Ulm, Germany

We carry out experiments with $^{87}\text{Rb}_2$ molecules in the rovibrational ground state of the $a^3\Sigma_u^+$ potential trapped in a 3d optical lattice. The molecules can be prepared in states with different angular momentum (either $N = 0$ or $N = 2$ with N being the molecular rotation). In the case of $N = 2$ the dimers are oriented along the direction of an external magnetic field. We can determine this orientation by measuring the molecular polarizability in an angle resolved way. By amplitude modulation of the lattice beams the excitation resonances from the lowest lattice band to higher bands are measured and the dynamical polarizability is inferred. In contrast to $N = 0$, where no angular dependence is found, $N = 2$ shows a significant change in polarizability as a function of angle between laser polarization and the molecular axis.

MO 14.2 Thu 10:45 BEBEL HS213

Spatially separating *para* and *ortho* water – fully quantum state selected samples of gas-phase molecules — ●DANIEL HORKE¹, YUAN-PIN CHANG¹, 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

Different molecular species present in supersonically expanded molecular beams can be separated using the electrostatic deflector, including different conformers [1], cluster stoichiometries [2], and individual quantum states of small linear rotor molecules [3].

We demonstrated the production of single quantum states of water in the gas-phase, and separation of its nuclear spin isomers. The spins of the two equivalent protons in water lead to two distinct nuclear spin states – *para* and *ortho*. According to the Pauli principle, the overall wavefunction of water must be antisymmetric for the exchange of the two protons. Due to the exact symmetry properties of water, *para* and *ortho* spin states correspond to distinct rovibronic states. We demonstrated the production of a cold beam of water, with >95% of population in the two absolute ground states. We spatially separated these using strong inhomogeneous electric fields. This is the first time pure samples of either spin isomer of water were produced.

[1] F. Filsinger *et al*, *Phys. Rev. Lett.* **100**, 133003; *ibid*, *Angew. Chem. Int. Ed.* **48**, 6900; Y.P. Chang *et al*, *Science* **342**, 98

[2] S. Trippel *et al*, *Phys. Rev. A* **86**, 033202

[3] J. H. Nielsen *et al*, *Phys. Chem. Chem. Phys.* **13**, 18971

MO 14.3 Thu 11:00 BEBEL HS213

Thermometry of Cold Trapped Molecular Anions in Multipole RF-Ion Traps — ●DANIEL HAUSER, SEUNGHYUN LEE, OLGA LAKHMANSKAYA, ERIC ENDRES, SUNIL KUMAR, THORSTEN BEST and ROLAND WESTER — Universität Innsbruck, Institut für Ionenphysik und Angewandte Physik, Österreich

The fast evolution in the fields of high precision spectroscopy and ion trapping during the last decades made it possible to gain high control of large quantum systems [1]. However, applying experimental methods as laser cooling and sympathetic cooling to more complex systems like molecules is difficult [2,3]. On the other hand, the development of multipole RF ion traps during the last 20 years made it possible to provide a large field free region which leads to weaker RF-heating as compared to low order Multipoles. Buffer gas cooling can be used to thermalize external as well as internal degrees of freedom of trapped

molecular ions. By carrying out rotationally resolved photodetachment spectroscopy of cold trapped OH^- molecule, we have employed a new way of measuring rotational temperatures [4]. In this work, we apply this new scheme of measuring rotational and translation temperature by doing photodetachment spectroscopy on OD^- . As an outlook, we present the status of rotational action THz spectroscopy of trapped molecular anions. This will give us new insight on rethermalisation processes and inelastic collision dynamics.

[1] T. Monz *et. al.*, *PRL* **106**, 130506 (2011) [2] A. Ostendorf *et. al.*, *PRL* **97**, 243005 (2006) [3] P. Staunum *et. al.*, *Nat.Phys.* **6**, 271-274 (2010) [4] R. Otto. *et. al.*, *PCCP* **15**, 612-18 (2013)

MO 14.4 Thu 11:15 BEBEL HS213

Spectroscopy of Cold RbSr Molecules Formed on Helium Nanodroplets — ●FLORIAN LACKNER, GÜNTER KROIS, JOHANN V. POTOTSCHNIG, THOMAS BUCHSTEINER, and WOLFGANG E. ERNST — Institute of Experimental Physics, Graz University of Technology, Petersgasse 16, A-8010 Graz, Austria

We report on the first spectroscopic investigation of the RbSr molecule. The molecules are prepared in their vibronic ground state in a sequential pickup process on the surface of helium nanodroplets, confined in a cold (0.38 K) and weakly perturbing superfluid environment. Based on our seminal work on LiCa [1], we extend our studies to the previously unobserved RbSr molecule, the most promising candidate for the creation of ultracold polar alkali-alkaline earth molecules. Utilizing resonance-enhanced multi-photon ionization time-of-flight (REMPI-TOF) spectroscopy and laser induced fluorescence (LIF) spectroscopy our investigations cover the spectral regime of 11500 cm^{-1} - 16500 cm^{-1} . The weak interaction between molecules and helium droplets causes a broadening of observed transitions. For spectrally resolved band systems the helium droplet isolation approach facilitates the determination of molecular constants. Our assignment is assisted by theoretical calculations of potential energy curves based on a multireference configuration interaction (MRCI) approach. Several strong transitions could be identified; the most prominent spectral feature is a vibrational resolved band system at 14000 cm^{-1} .

[1] G. Krois, J.V. Pototschnig, F. Lackner and W.E. Ernst, *J. Phys. Chem. A*, DOI: 10.1021/jp407818k (2013)

MO 14.5 Thu 11:30 BEBEL HS213

Transverse Focusing Effects in the Zeeman Deceleration of Hydrogen Atoms — ●KATRIN DULITZ¹, ATREJU TAUSCHINSKY¹, MICHAEL MOTSCH², NICOLAS VANHAECKE^{3,4}, and TIMOTHY P. SOFTLEY¹ — ¹Department of Chemistry, University of Oxford, Chemistry Research Laboratory, Mansfield Road, Oxford, OX1 3TA, UK — ²Laboratorium für Physikalische Chemie, ETH Zürich, Wolfgang-Pauli-Straße 10, 8093 Zürich, Switzerland — ³Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany — ⁴Laboratoire Aimé Cotton, CNRS, Université Paris-Sud, ENS Cachan, 91405 Orsay, France

Zeeman deceleration is an experimental technique in which inhomogeneous, time-dependent magnetic fields inside an array of solenoid coils are used to manipulate the velocity of a supersonic beam [1, 2]. We have built and characterised a 12-stage Zeeman decelerator for hydrogen atoms in Oxford. We present experimental results illustrating that the overall acceptance in a Zeeman decelerator can be significantly increased by applying a low, anti-parallel magnetic field to one of the coils so as to form a temporally varying quadrupole field which improves transverse particle confinement [3]. The results show excellent agreement with three-dimensional numerical particle trajectory simulations, and they suggest the use of a modified coil configuration to improve transverse focusing during the deceleration process.

[1] N. Vanhaecke *et al.*, *Phys. Rev. A* **75**, 031402 (2007). [2] E. Narevi-

cius et al., Phys. Rev. A **77**, 051401 (2008). [3] K. Dulitz, M. Motsch, N. Vanhaecke, T. P. Softley, *submitted*.

MO 14.6 Thu 11:45 BEBEL HS213

Kolmogorov-type scaling at a non-thermal fixed point in two dimensional Bose gases — ●THORGE MÜLLER^{1,2}, MARKUS KARL^{1,2}, and THOMAS GASENZER^{1,2} — ¹Institut für Theoretische Physik, Ruprecht-Karls-Universität Heidelberg, Philosophenweg 16, 69120 Heidelberg — ²ExtreMe Matter Institute EMMI, GSI Helmholtzzentrum für Schwerionenforschung GmbH, Planckstraße 1, 64291 Darmstadt, Germany

We present a numerical analysis of non-thermal fixed points in ultracold Bose gases in two spatial dimensions. Imprinting of multiply quantized vortices is used to drive the system far away from equilibrium. We demonstrate that the ensuing dynamical evolution leads the system towards a quasi-stationary state showing non-thermal scaling solutions in the occupation number, known as non-thermal fixed points. We provide numerical evidence that the employed driving scheme realizes a new scaling solution in the infrared, $n(k) \sim k^{-5}$. Our result has been predicted by analytical calculations, however it has not been observed numerically up to now. We discuss this solution's connection to steady energy fluxes in the infrared regime in momentum space and to vortex clustering in real space. Also, we show that the latter leads to almost-classical superfluid flow patterns giving rise to interpret the derived scaling solution as being closely related to the Kolmogorov scaling law.

MO 14.7 Thu 12:00 BEBEL HS213

Hybrid atom-ion trap for sympathetic cooling of OH⁻ ions by a rubidium MOT — ●JULIAN GLÄSSEL¹, BASTIAN HÖLTKEMEIER¹, HENRY LOPEZ¹, PASCAL WECKESSER¹, THORSTEN BEST², ERIC ENDRES², ROLAND WESTER², and MATTHIAS WEIDEMÜLLER¹ — ¹Physikalisches Institut, Im Neuenheimer Feld 226, 69120 Heidelberg — ²Institut für Ionenphysik und Angewandte Physik, Technikerstraße 25/3, 6020 Innsbruck

Ultracold molecules can be created either from associating ultracold atoms or by trapping and sympathetically cooling them. We report on

the status of a new setup employing a hybrid atom-ion trap that allows to sympathetically cool OH⁻ ions by ultracold rubidium. A wide range of other ion species can also be used, making the setup very versatile.

Our setup consists of an octupole rf-trap of thin wires that has a large field-free region while allowing enough optical access to overlay a magneto optical trap inside. A dark spontaneous force optical trap (darkSPOT) configuration is used to bring most rubidium to the ground state, hence avoiding ion loss by inelastic collisions, as well as allowing higher densities up to 3×10^{11} atoms/cm³ to enhance the interaction rate. Simulations of ion trajectories inside the ultracold rubidium cloud suggest sympathetic cooling by at least one order of magnitude.

MO 14.8 Thu 12:15 BEBEL HS213

Cavity cooling of free nanoparticles in high vacuum — ●STEFAN KUHN, PETER ASENBAUM, STEFAN NIMMRICHTER, UGUR SEZER, and MARKUS ARNDT — Faculty of Physics, VCQ, University of Vienna, Boltzmanngasse 5, Vienna A-1090, Austria

Resonant laser cooling techniques have given a great boost to the field of atomic physics throughout the last 30 years. Complex molecules and nanoparticles, however, cannot yet be controlled by these methods due to the lack of addressable cyclic transitions. In reply to this need, cavity cooling has been proposed more than 15 years ago [1, 2] and was recently realised experimentally with nanoparticles [3,4]. In this talk we will present our experimental results on transverse cavity cooling of free silicon nanoparticles in high vacuum [4]. We produce and launch them under high vacuum conditions such that they transit a high finesse optical cavity without any perturbation by a buffer gas. From the scattered light of the particles we can trace their dynamics in real time. We discuss modifications which are currently being set up to improve the cooling rate of the system. These advances will be crucial for future quantum coherence experiments with very massive nanoparticles[5].

- [1] P. Horak et al., Phys. Rev. Lett., 79 (1997)
- [2] V. Vuletic & S. Chu, Phys. Rev. Lett., 84 (2000)
- [3] N. Kiesel et al., PNAS 110 (2013)
- [4] P. Asenbaum et al., Nat. Commun. 4:2743 (2013)
- [5] K. Hornberger et al., Rev. Mod. Phys., 84 (2012)

MO 15: Experimental Techniques 3

Time: Thursday 10:30–12:15

Location: BEBEL SR144

MO 15.1 Thu 10:30 BEBEL SR144

Characterisation of dinuclear transition metal complexes by collision-induced dissociation studies and IRMPD spectroscopy — ●MAXIMILIAN GAFFGA, JOACHIM HEWER, JOHANNES LANG, ISABEL MUNSTEIN, WERNER THIEL, and GEREON NIEDNER-SCHATTEBURG — Technische Universität Kaiserslautern, Deutschland

In extension of previous work [1], a combination of mass spectrometric and spectroscopic techniques was applied to determine the composition and structure of isolated cationic dinuclear transition metal containing complexes in the gas phase. Via the electrospray ionization technique the dinuclear metal complexes could be transferred into the gas phase and then stored in a Paul trap.

Collision-induced dissociation (CID) studies were used to get information about the fragmentation behavior of the complexes. Assignment of vibrational bands and identification of the complex coordination pattern arise from comparison of Infrared Multiple Photon Dissociation (IRMPD) spectra in the range of 1200 - 4000 cm⁻¹ to calculated spectra (B3LYP/cc-pvDZ,ECP). Seemingly surprising fragmentation patterns are well understood on the basis of these investigations.

References: [1] Nosenko, Y.; Menges, F.; Riehn, C.; Niedner-Schatteburg, G. Phys. Chem. Chem. Phys. 2013, 15, 8171.

MO 15.2 Thu 10:45 BEBEL SR144

Photofragmentation imaging of vibrationally excited methyl iodide — ●ALEXANDER DÖRFLER, MARTIN STEI, EDUARDO CARRASCOA, and ROLAND WESTER — Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck

In our group a crossed-beam velocity map imaging setup has been developed to study ion molecule reactions [1]. To study the effect of vibrational C-H symmetric stretch ($v_1=1$) excitation on the dynamics and kinematics of the reaction CH₃I + F⁻ a narrowband IR-Laser sys-

tem has been set up. To characterize and optimize the vibrational excitation in a CH₃I molecular beam, we have applied a probing scheme based on the approach of Zhou and coworkers [3]. The basic idea is, that since the v_1 vibrational excitation is mainly a spectator to the dissociation process, the initially excited CH₃I can be studied by probing CH₃ produced by photodissociation. In this contribution we will be present high resolution velocity images and kinetic energy distribution of the two different CH₃ fragments ($v_1=0$ and $v_1=1$) produced by photodissociation at 266 nm ionized using a (2+1) REMPI scheme. We will compare our results to the work of Zhou et al. [2], who applied a different dissociation wavelength. Furthermore, an approach to measure rotational beam temperatures with this scheme will be discussed.

- [1] R. Wester, Phys. Chem. Chem. Phys. 16, 396 (2013) [2] Hu, L., Z. Zhou, C. Dong, L. Zhang, Y. Du, M. Cheng and Q. Zhu, J. Phys. Chem. A 117(21): 4352-4357 (2013)

MO 15.3 Thu 11:00 BEBEL SR144

Prediction of Infra-Red spectra of organic liquids within the framework of the cluster model for a substance — GENNADY MELNIKOV¹, ●VYACHESLAV VERVEYKO², EUGENE POSTNIKOV², and MARINA VERVEYKO² — ¹South West State University — ²Kursk State University

The distribution function of clusters on particles number is proposed within the frame of the cluster model of a fluid condensed state. The estimations of the most probable, average and root-mean-square number of particles in clusters are obtained using the proposed cluster distribution for simple and organic liquids as a function of the thermodynamic parameters.

The relation for the prediction of frequencies in the infra-red (IR) spectrum of liquids is connected with the presence of rotational and oscillatory motions in clusters structure accordingly to the effective field theory. Verification of the proposed model has been evaluated for

inert gases, nitrogen, oxygen, hydrocarbons and water.

The comparison of the calculated results with the experimental data confirms a relevance of the proposed model for the prediction of a number of particles, which form clusters and frequencies of the IR-spectra for liquids.

G.A. Melnikov, V.N. Verveyko et al. *Int. J. Therm.* 32 (2011), 901.

G.A. Melnikov, V.N. Verveyko et al. *High Temperature.* 50 (2012), 214.

MO 15.4 Thu 11:15 BEBEL SR144

Methods to simulate light propagation and optical response in small metal cluster aggregates — ●POLINA LISINETSKEYA¹ and ROLAND MITRIC² — ¹Fachbereich Physik, Freie Universität Berlin, Arnimallee 14, D-14195 Berlin, Deutschland — ²Institut für Physikalische und Theoretische Chemie, Universität Würzburg, D-97074 Würzburg, Deutschland

We present a method of the simulation of the optical response and light propagation in ordered arrays of small noble-metal clusters with discrete electronic structure. The description of the systems is based on the excitonic Hamiltonian constructed employing the TDDFT electronic states of the individual subunits and the dipole-dipole interaction between them. The time evolution of the systems is studied by numerical solution of the time-dependent Schrödinger equation with the excitonic Hamiltonian perturbed by an external laser field. For each subunit the time-dependent dipole moment is calculated using the reduced density matrix formalism. Such quantum-mechanically determined dipole moments are used to simulate the spatio-temporal distribution of the electric field produced by the array. Additionally, we introduce an approximate self-consistent iterative approach to treat arrays consisting of many subunits. The developed methodology is illustrated first on the example of Ag₂ and Ag₈ cluster pairs. Subsequently, light propagation in a triangular-shaped array consisting of six Ag₈ clusters is simulated. Finally, the possibility of optimal control of light propagation in a T-shaped structure formed of seven Ag₈ clusters is demonstrated.

MO 15.5 Thu 11:30 BEBEL SR144

Characterization of metal carbonyls and their release of carbon monoxide using IR absorption spectroscopy — ●MORITZ KLEIN¹, UTE NEUGEBAUER^{1,2}, ALI GHEISARI¹, MICHAEL SCHMITT³, and JÜRGEN POPP^{1,2,3} — ¹Leibniz Institute of Photonic Technology, Jena, Germany — ²Center for Sepsis Control and Care, Jena University Hospital, Germany — ³Institute of Physical Chemistry and Abbe Center of Photonics, Friedrich Schiller University of Jena, Germany

Carbon monoxide (CO) is a poisonous gas, but nevertheless, application of low doses of CO in medical treatment has been proven several beneficial effects on health. Novel compounds, mainly metal carbonyl complexes, have been synthesized that liberate CO in a controlled manner. However, their exact mechanism and kinetic of CO release is mostly not known. In this contribution, we applied different techniques of infrared (IR) absorption spectroscopy to study the decay of these metal carbonyls: IR gas phase spectroscopy is used to detect liberated CO in the supernatant gas phase above these compounds and attenuated total reflection (ATR) IR spectroscopy of solutions is applied to directly observe the decay of the carbonyl groups of the solved educt. Molecules with different CO releasing mechanisms were investigated. Following their CO release in a time-resolved manner and analysis of their end products supported by DFT calculations yielded important insights into their reaction mechanisms.

Acknowledgement: Financial support by DFG (FOR 1738) and BMBF (CSCC) is highly acknowledged as well as the group of M. Westerhausen for metal carbonyl syntheses.

MO 15.6 Thu 11:45 BEBEL SR144

Characterization of a 6 K Ring-Electrode Ion-Trap used for IR Photodissociation Experiments in a Triple Mass Spectrometer — ●TIM ESSER¹, NADJA HEINE¹, and KNUT R. ASMIS^{1,2} — ¹Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin, Germany — ²Wilhelm-Ostwald-Institut für Physikalische und Theoretische Chemie, Universität Leipzig, Linnéstrasse 2, D-04103 Leipzig, Germany

Mass-selective infrared photodissociation (IR-PD) spectroscopy combined with electronic structure calculations, is currently one of the most generally applicable techniques to determine the structure of gas phase cluster ions. To assure that the clusters are in their vibrational ground state they are typically buffer-gas cooled in a cryogenic ion trap. Here, we focus on the characterization of a linear ring-electrode radio-frequency (rf) ion-trap used in a 6K ion trap triple mass spectrometer. Preliminary results on the partially rotationally-resolved IR-PD spectrum of the singly hydrated ammonium ion, NH₄⁺(H₂O), allow to determine the rotational temperature as a function of the rf amplitude, buffer-gas pressure and store time. Apart from thermalization, the trap allows for bunching of the continuous ion beam and the attachment of messenger atoms or molecules. A genetic algorithm was developed, in order to automatically optimize the three sets of voltages, which are applied to the 12 pairs of ring electrodes during filling, storing and extraction. We further discuss the influence of the form of the trapping potential as well as the length of the store time on the size, shape and rotational temperature distribution of the ion packages.

MO 15.7 Thu 12:00 BEBEL SR144

Direct imaging of S_N2 pathways in the reaction F⁻ + CH₃Cl — ●EDUARDO CARRASCOSA, ADITYA KELKAR, MARTIN STEI, THORSTEN BEST, and ROLAND WESTER — Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck, Innsbruck, Austria

Halogenated hydrocarbons play a very important role in organic synthesis both as solvents and as reaction intermediates. The bimolecular nucleophilic substitution (S_N2) is one of the most common reactions of these compounds. Using a crossed beam setup and a velocity map imaging spectrometer our group has extensively studied exothermic S_N2 reaction systems [1]. The present study focuses on the dynamics of the reaction between fluorine anions, F⁻, and methyl chloride, CH₃Cl.

In this presentation velocity distributions of the product Cl⁻ ion at different relative collision energies ranging from 0.6 eV to 2.5 eV will be shown. The direct S_N2 pathway is the dominant channel at high energies, with an increasingly strong contribution from the complex mediated channel at lower energies. The experimental results will be compared with recent theoretical calculations on this system[2,3]. Moreover, a comparison with previous studies by our group on similar systems like Cl⁻ + CH₃I and F⁻ + CH₃I [4], will provide a better understanding of the dynamical factors in S_N2 reactions.

[1] R. Wester, *PCCP*, **16**, 396 (2014) [2] A.P. Bento and F.M. Bickelhaupt, *J. Org. Chem.*, **73**(18), 7290 (2008) [3] M. Mugnai et al., *J. Chem. Phys.*, **118**, 2767 (2003) [4] J. Mikosch et al., *J. Am. Chem. Soc.*, **135**, 4250 (2013)

MO 16: Atomic clusters (with A)

Time: Thursday 10:30–12:30

Location: BEBEL E44/46

Invited Talk

MO 16.1 Thu 10:30 BEBEL E44/46

Unusual electron dynamics in He clusters induced by intense XUV pulses — ●YEVHENYI OVCHARENKO¹, AARON LAForge², VICTOR LYAMAYEV³, RAPHAEL KATZY², PATRICK O'KEEFFE⁴, OKSANA PLEKAN⁵, PAOLA FINETTI⁵, ROBERT RICHTER⁵, KEVIN PRINCE⁵, MARCEL DRABELLS⁶, CARLO CALLEGARI⁵, FRANK STIENKEMEIER², and THOMAS MÖLLER¹ — ¹IOAP, TU-Berlin, Germany — ²Physikalisches Institut, Universität Freiburg, Germany — ³European XFEL, Hamburg, Germany — ⁴CNR IMP, Monterotondo Scalo, Italy — ⁵Elettra-Sincrotrone Trieste, Basovizza, Italy — ⁶EPFL, Lausanne, Switzerland

The investigation of complex atomic and molecular systems in intense IR and XUV pulses has attracted considerable attention during the last decade, since it leads to a better understanding of light-matter interaction. Recently, the first seeded Free Electron Laser FERMI became available for users and now offers unique possibilities to perform detailed investigations in such systems due to the narrow bandwidth, fine energy tunability and high intensity in the XUV energy range. By using this new source the ionization dynamics in He clusters has been explored with electron spectroscopy in a wide energy range. In addition to the conventional sequential multi-step ionization with a photon energy well above the first ionization potential (IP) a novel ionization

process following resonant excitation below IP was observed. It is due to autoionization of two or more electronically excited cluster atoms as predicted recently [1]. The process is very efficient and can exceed the rate of direct photoionization above IP.[1] A.I. Kuleff et al., PRL 105, 043004 (2010)

MO 16.2 Thu 11:00 BEBEL E44/46

Detecting interatomic Coulombic decay in neon clusters by photon measurement — ●ANDREAS HANS¹, A. KNE¹, M. FÖRSTEL², P. SCHMIDT¹, P. REISS¹, T. JAHNKE³, R. DÖRNER³, A. I. KULEFF⁴, L. S. CEDERBAUM⁴, P. V. DEMEKHIN¹, U. HERGENHAHN², and A. EHRESMANN¹ — ¹Institut f. Physik, Universität Kassel, Heinrich-Plett-Str. 40, 34132 Kassel — ²Max-Planck-Institut f. Plasmaphysik, c/o HZB-Bessy II, Albert-Einstein Str. 15, 12489 Berlin — ³Institut f. Kernphysik, Goethe Universität, Max-von-Laue-Str. 1, 60438 Frankfurt — ⁴Physikalisch-Chemisches Institut, Universität Heidelberg, Im Neuenheimer Feld 229, 69120 Heidelberg

The role of interatomic Coulombic decay (ICD) in biological context is currently discussed due to anticipated genotoxic effects of low energy electrons typically produced in non-local autoionization processes. All unambiguous experimental observations of ICD so far relied on the detection of charged decay products. The further investigation of the biological relevance by this methods is constrained, since the mean free travel path of charged particles in dense media (e.g. biological samples) usually is very short. A complementary detection method for ICD, applicable to dense media, is therefore required. Here, we report the first unequivocal proof of ICD by measurements of fluorescence emission from neon clusters. In a proof of principle experiment, photon and electron emission of a supersonic neon cluster jet were measured simultaneously. Furthermore it is shown that the photon signal of clusters can easily be discriminated from the monomer's signal by its characteristic resonant excitation energies and lifetime measurements.

MO 16.3 Thu 11:15 BEBEL E44/46

Electron re-localization dynamics in Xenon clusters under intense XUV pump-probe excitation — ●M. ARBEITER, CH. PELTZ, and TH. FENNEL — Institute of Physics, University of Rostock

Intense and temporally structured light fields from free-electron lasers enable the time-resolved investigation of ionization dynamics in finite systems at shortwavelength, as demonstrated in a recent femtosecond XUV pump-probe experiment on Xenon clusters [1] at FLASH. Sub-picosecond relaxation dynamics in the XUV driven cluster nanoplasma are revealed via the delay dependent charge states of emitted atomic ions. Our semiclassical molecular dynamics study reveals that the process of electron re-localization in the ionized cluster is key to understand the delay-dependent ion charge states [2]. We show that nanoplasma expansion cooling rapidly diminishes three-body-recombinations within a few picoseconds leading to a bimodal electron energy distribution of strongly bound electrons (re-localized) and weakly bound (quasifree, Rydberg-like). A suitable criterion to account for electron re-localization is found by microscopic analysis of the local quasi continuum between neighboring atoms, leading to an appropriate definition of effective ion charge states. A systematic pump-probe analysis reveals that electron re-localization provides a fingerprint of electron cooling and nanoplasma rarefaction through cluster expansion and yield a good qualitative agreement with the observed experimental findings [1].

[1] M. Krikunova et al. J. Phys. B 45, 105101 (2012)

[2] M. Arbeiter, Ch. Peltz, Th. Fennel, to be submitted

MO 16.4 Thu 11:30 BEBEL E44/46

Explosion of heteronuclear clusters irradiated by strong X-ray pulses — ●PIERFRANCESCO DI CINTIO, ULF SAALMANN, and JAN-MICHAEL ROST — Max Planck Institute for the Physics of Complex Systems, Nöthnitzer Straße 38, 01187 Dresden, Germany

By means of N-body simulations we study the ion and electron dynamics in molecular first-row hydride clusters when exposed to intense and short X-ray pulses [1]. We find that, for a particular range of X-ray intensities, fast protons are ejected from the system on a considerably shorter time scale than that of the screened core. As a consequence, the structure of heavy atoms is kept "intact", which may be relevant in the context of X-ray based molecular imaging. Moreover the final charge states of the heavy ions are considerably lower than those of the ions in pristine atomic clusters exposed to the same laser pulses, which is in agreement with recent measurement of CH₄ cluster at the LCLS in Stanford.

[1] P. Di Cintio, U. Saalman & J.M. Rost, Phys. Rev. Lett. 111,

3401 (2013)

MO 16.5 Thu 11:45 BEBEL E44/46

THz field streaking implemented to studies of rare gas clusters — ●T OELZE¹, B SCHÜTTE², M MÜLLER¹, J P MÜLLER¹, M SAUPPE¹, L FLÜCKIGER¹, D RUPP¹, M WIELAND³, U FRÜHLING³, A AL-SHEMMARY⁴, N STOJANOVIC⁴, T MÖLLER¹, M DRESCHER³, and M KRIVONOVA¹ — ¹IOAP TU Berlin — ²MBI — ³IEXP Uni Hamburg — ⁴HASYLAB@DESY

Coherent, ultrashort and high flux photon pulses in the short-wavelength regime from free-electron lasers enable a wide range of experiments to study the interaction between light and matter with high spacial and temporal resolution. In our experiment at FLASH rare gas clusters were used as size-scalable model systems and were irradiated by XUV pulses at 92 eV in the presence of a THz field. At the beginning of the FEL pulse photoionized electrons escape the cluster leaving a positive charge behind. As a result further electron emission becomes frustrated and an electron nanoplasma is formed. Field-driven streaking camera allows to study how the temporal structure of the electron photoemission is altered by the cluster environment. In this approach the momentum of emitted electrons is changed according to the phase of the electric field of the THz radiation. Photoelectron spectra taken at different phases of the THz field are then used to create streaking spectrograms. From these spectrograms the temporal structure of the electron photoemission can be reconstructed providing insight into the nanoplasma formation.

MO 16.6 Thu 12:00 BEBEL E44/46

Laser-induced delayed electron emission of metal cluster anions — ●CHRISTIAN BREITENFELDT¹, KLAUS BLAUM², SEBASTIAN GEORGE², MICHAEL LANGE², SEBASTIAN MENK², CHRISTIAN MEYER², LUTZ SCHWEIKHARD¹, and ANDREAS WOLF² — ¹Institut für Physik, Ernst-Moritz-Arndt Universität, 17487 Greifswald, Germany — ²Max-Planck-Institut für Kernphysik, Saupfercheckweg 1, 69117 Heidelberg, Germany

Radiative cooling is a fundamental process that determines the internal temperature of vibrationally excited ions as a function of time, eventually bringing them into thermal equilibrium with their environment. We have investigated the cooling of Cu_n⁻ (n=4,5,6,7) and Co_n⁻ (n=3,4) anions in a cryogenic electrostatic trap. The cluster ions were produced in a Cs sputter ion source, with a vibrational excitation corresponding to temperatures of several thousand Kelvins. They were then size-selected and transferred to the Cryogenic Trap for Fast ion beams CTF located at the Max-Planck-Institut für Kernphysik within 120 μs. They were stored at a kinetic energy of 6 keV. This electrostatic ion beam trap can be operated at a temperature below 15 K by a closed-cycle helium refrigeration system. The extremely low pressure (few 10⁻¹² mbar) achieved by cryopumping resulted in a very low background of collision-induced ion loss and thus a beam lifetime of several minutes. We have studied vibrational autodetachment (also called delayed detachment) by recording the rate of neutral particles escaping from the trap as a function of the delay after the pulses from a laser emitting at wavelengths of 600 to 1300 nm.

MO 16.7 Thu 12:15 BEBEL E44/46

Real-time observation of recombination in clusters exposed to intense HHG pulses — ●BERND SCHÜTTE¹, MATHIAS ARBEITER², THOMAS FENNEL², FILIPPO CAMPI³, MARC J. J. VRAKKING¹, and ARNAUD ROUZÉE¹ — ¹Max-Born-Institut, Berlin, Germany — ²Universität Rostock, Germany — ³Lund University, Sweden

High-order harmonic generation (HHG) sources provide light pulses in the extreme-ultraviolet (XUV) spectral range with unique properties including a large wavelength tunability, extremely short pulses down to the attosecond range and a straightforward manner in which pump-probe measurements can be performed. Here we demonstrate that the advantageous features of HHG in combination with the velocity map imaging (VMI) technique lead to a significant improvement in the understanding of cluster dynamics.

The observation of very low kinetic energy electrons from rare-gas clusters exposed to intense HHG pulses is attributed to electron-ion recombination processes to Rydberg states in the expanding nanoplasma. Their subsequent reionization with the DC detector electric field known as frustrated recombination is observed experimentally for the first time. Moreover, using a time-delayed visible or infrared pulse, we investigate the recombination dynamics of quasifree electrons to atomic excited states during the nanoplasma expansion, a method termed

reionization of excited atoms from recombination (REAR). In addition, we show that REAR can be used as a sensitive probe for tracing

the cluster expansion up to the nanosecond range.

MO 17: Excitons and Excitation Transfer (SYET 2)

Time: Thursday 14:00–15:30

Location: BEBEL HS213

Invited Talk

MO 17.1 Thu 14:00 BEBEL HS213

Non-adiabatic relaxation dynamics in perylene bisimide dimers excited by femtosecond laser pulses — ●VOLKER ENGEL¹, BERND ENGELS¹, MIRJAM FALGE¹, MARTIN KESS¹, STEFAN LOCHBRUNNER², ALEXANDER SCHUBERT¹, VOLKER SETTELS¹, WALTER STRUNZ¹, and FRANK WÜRTHNER³ — ¹Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Emil-Fischer-Str. 42, 97074 Würzburg, Germany — ²Institut für Physik, Universität Rostock, Universitätsplatz 3, 18055 Rostock, Germany — ³Institut für Organische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

We present a model for the relaxation dynamics in perylene bisimide dimers which is based on ab-initio electronic structure and quantum dynamics calculations including effects of dissipation. The excited state dynamics proceeds via a mixing of electronic states of local Frenkel and charge-transfer characters which becomes effective upon a small distortion of the dimer geometry. In this way it is possible to explain the fast de-population of the photo-excited state as seen in femtosecond transient absorption measurements. This hints at a trapping mechanism which involves non-adiabatic and dissipative dynamics in an excited state vibronic manifold.

MO 17.2 Thu 14:30 BEBEL HS213

Hopping transport of excited states in polymeric carbon nitride photocatalysts — ●CHRISTOPH MERSCHJANN^{1,2}, STEFANIE TSCHIERLEI¹, STEFAN LOCHBRUNNER¹, TOBIAS TYBORSKI^{2,3}, ARNE THOMAS⁴, and THOMAS SCHEDEL-NIEDRIG³ — ¹Institut für Physik, Universität Rostock, D-18051 Rostock, Germany — ²Max-Born-Institut für Nichtlineare Optik und Kurzzeitspektroskopie, D-12489 Berlin, Germany — ³Helmholtz-Zentrum Berlin, D-14109 Berlin, Germany — ⁴Technische Universität Berlin, D-10623 Berlin, Germany

The spectral and temporal development of optically excited states in polymeric carbon nitride (PCN) photocatalysts is investigated using time-resolved optical spectroscopy. By combining transient absorption results from a femtosecond pump-probe setup and transient photoluminescence using streak-camera and time-resolved single-photon counting investigations, the visible radiative emission upon UV excitation is obtained.

It is found that the decay of the emission exhibits a non-exponential behaviour over more than six decades in time (150 fs to 500 ns).

This characteristic points to a diffusive transport of localized excited states (Frenkel excitons). The underlying incoherent hopping transfer bears strong similarities to a small polaron transport. The consequences of such a comparably slow kind of transport for the catalytic activity of PCN are discussed.

MO 17.3 Thu 14:45 BEBEL HS213

Exciton coupling effects in polymeric cis-indolenine squaraine dyes — ●FEDERICO KOCH¹, SEBASTIAN VÖLKER², CHRISTOPH LAMBERT², 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

Polymeric cis-indolenine squaraine (pSQ) dye compounds display a

broad absorption in the red-to-NIR region with distinct maxima but a narrow fluorescence. The energetic shifts of the absorption maxima corresponding to the monomer can be explained by a mixture of H- and J-type alignment of chromophores [1].

We investigated the exciton coupling of pSQ in DCM (predominantly J-type alignment) and DMF (predominantly H-type alignment) by femtosecond transient absorption (TA) and coherent two-dimensional (2D) spectroscopy. In the TA studies we observed ultrafast relaxation dynamics ranging from fs to ns. The fast dynamics probably relate to an excitonic coupling. With 2D spectroscopy we aim at the direct characterization of the coupling and the corresponding interaction between the excitonic states.

[1] S. F. Völker, and C. Lambert, Chem. Mat. 2012, 24, 2541-2553

MO 17.4 Thu 15:00 BEBEL HS213

Vibronic speed-up of the excitation energy transfer in the Fenna-Matthews-Olson complex — ●PETER NALBACH, CESAR A. MUJICA-MARTINEZ, and MICHAEL THORWART — I. Institut für Theoretische Physik, Universität Hamburg, Jungiusstr. 9, 20355 Hamburg

We show that the efficient excitation energy transfer in the Fenna-Matthews-Olson molecular aggregate under realistic physiological conditions is fueled by underdamped vibrations of the embedding proteins. For this, we present numerically exact results for the quantum dynamics of the excitons in the presence of nonadiabatic vibrational states in the Fenna-Matthews-Olson aggregate employing an environmental fluctuation spectral function derived from experiments. Assuming the prominent 180 cm⁻¹ vibrational mode to be underdamped, we observe, on the one hand, besides vibrational coherent oscillations between different excitation levels of the vibration also prolonged electronic coherent oscillations between the initially excited site and its neighbours. On the other hand, however, the underdamped vibrations provide additional channels for the excitation energy transfer and by this increase the transfer speed by up to 30% . (ArXiv:1311.6363)

MO 17.5 Thu 15:15 BEBEL HS213

Temperature-dependent femtosecond time-resolved pump-probe study of exciton dynamics in (6,5) SWNTs — ●CHRISTOPH MANN and TOBIAS HERTEL — Julius-Maximilians-Universität Würzburg, Institut für Physikalische und Theoretische Chemie, Würzburg

Single wall carbon nanotubes (SWNTs) can be thought of as one-dimensional (1D) nanostructures consisting of rolled-up graphene sheets. Because of their unique electronic, mechanical and optical properties, an understanding of the exciton dominated excited-state dynamics in SWNTs is of great interest for both, better insight into fundamental photophysics of 1D systems in complex environments and for optoelectronic applications. We studied the temperature dependence of femtosecond transient absorption kinetics. In addition we carried out time-resolved and steady-state photoluminescence investigations between room temperature and 14 K. The combined information from these experiments provides new insights into the coupling of bright and dark excitonic states as well as on the temperature dependence of radiative and nonradiative processes.

MO 18: Theory 3: Quantum Chemistry

Time: Thursday 14:00–15:45

Location: BEBEL SR144

MO 18.1 Thu 14:00 BEBEL SR144

Auger decay of double core holes in small linear molecules — ●LUDGER INHESTER¹, GERRIT GROENHOF², and HELMUT GRUBMÜLLER¹ — ¹Max Planck Institut für biophysikalische Chemie, Göttingen — ²Universität Jyväskylä

Because of its high intensity X-FEL light is able to sequentially photo-

ionize multiple core electrons and thus enables one to probe molecules with multiple core holes. Using quantum mechanical ab-initio methods we have investigated the Auger decay of single and double core hole states in small linear molecules, such as acetylene, nitrogen and carbon-monoxide. In our approach we use multi-reference configuration interaction calculation for the bound electrons while the electronic

continuum is represented via the single center method, in which the continuum electron is expanded on a radial grid with spherical harmonics[1,2]. We find that the decay rate depends on where the core vacancies are located and that the highest decay rate is obtained if two vacancies are located on the same nucleus. This result is explained by the core hole induced rearrangements of the valence electronic structure. The implications of our findings for single molecule diffractive imaging application with X-FEL's will be discussed.

[1] Inhester et al., JCP 136, 144304 (2012) [2] Inhester et al., JCP 138, 164304 (2013)

MO 18.2 Thu 14:15 BEBEL SR144

Exact Factorization of the Electron-Nuclear Wavefunction: Exact Electronic Potentials in Coupled Electron-Ion Dynamics — ●YASUMITSU SUZUKI¹, ALI ABEDI¹, NEIPA MAITRA², KOICHI YAMASHITA³, and E. K. U. GROSS¹ — ¹Max Planck Institute of Microstructure Physics, Weinberg 2, D-06120 Halle, Germany — ²Department of Physics and Astronomy, Hunter College and the City University of New York, 695 Park Avenue, New York, New York 10065, USA — ³Department of Chemical System Engineering, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

We develop a novel approach to the coupled motion of electrons and ions that focuses on the dynamics of the electronic subsystem. Usually the description of electron dynamics involves an electronic Schrödinger equation where the nuclear degrees of freedom appear as parameters or as classical trajectories. Here we derive the exact Schrödinger equation for the subsystem of electrons, staying within a full quantum treatment of the nuclei. This exact Schrödinger equation features a time-dependent potential energy surface for electrons (e-TDPES). We demonstrate that this exact e-TDPES differs significantly from the electrostatic potential produced by classical or quantum nuclei.

[1] Y. Suzuki, A. Abedi, N. T. Maitra, K. Yamashita and E. K. U. Gross, e-print arXiv:1311.3218v1

MO 18.3 Thu 14:30 BEBEL SR144

Exact factorization of the electron-nuclear wave function: Applications — ●FEDERICA AGOSTINI — Max Planck Institute of Microstructure Physics, Halle, Germany

The exact factorization [1] of the molecular wave function offers a new perspective on the correlated dynamics of electrons and nuclei. In particular, the Hamiltonian generating the nuclear evolution contains time dependent vector and scalar potentials. These potentials are uniquely defined, up to within a gauge transformation, and govern nuclear dynamics, yielding the nuclear wave function. They represent the exact electronic effect on the nuclei.

This reformulation of the time dependent Schroedinger equation is the starting point for the development of approximations, consisting in the classical treatment of only the nuclear degrees of freedom. With this objective in mind, we investigate the properties of the potentials in a model for proton coupled electron transfer. The exact solution of the full quantum mechanical problem gives access to the scalar potential [2,3], in a gauge where the vector potential is zero. We study the features of the potential and we test the performance of the classical approximation, given that the exact effect of the electrons on the nuclei is known.

[1] A. Abedi, N.T. Maitra and E.K.U. Gross, Phys. Rev. Lett. 105 (2010); J. Chem. Phys. 137 (2012) [2] A. Abedi, F. Agostini, Y. Suzuki and E.K.U. Gross, Phys. Rev. Lett. 110 (2013) [3] F. Agostini, A. Abedi, Y. Suzuki and E.K.U. Gross, Mol. Phys. 111 (2013)

MO 18.4 Thu 14:45 BEBEL SR144

The exact time-dependent potential energy surface for the strong field dynamics of H_2^+ — ●ELHAM KHOSRAVI¹, ALI ABEDI², ALEJANDRO SAENZ¹, and E. K. U. GROSS² — ¹Institut für Physik, Humboldt-Universität zu Berlin, Newtonstraße 15, 12489 Berlin, Germany — ²Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, D-06120 Halle, Germany

It was recently shown [1,2] that the complete wave-function for a system of electrons and nuclei evolving in a time-dependent external potential can be exactly factorized into an electronic wave-function and a nuclear wave-function. The concepts of an exact time-dependent potential energy surface (TDPES) and exact time-dependent vector potential emerge naturally from the formalism. These potentials mediate the couplings between the nuclear and the electronic degrees of freedom in a formally exact way. In this framework, the nuclear dy-

namics is governed by a Schrödinger equation that contains a TDPES and a time-dependent vector potential. Here we study the concept of the exact TDPES for the H_2^+ molecular ion exposed to a laser field and demonstrate the significance of this concept as a powerful tool in analyzing multiphoton processes.

[1] Ali Abedi, Neepa T. Maitra, and E. K. U. Gross, Phys. Rev. Lett. 105, 123002 (2010)

[2] Ali Abedi, Neepa T. Maitra, and E. K. U. Gross, J. Chem. Phys. 137, 22A530 (2012)

MO 18.5 Thu 15:00 BEBEL SR144

Exact factorization of the time-dependent electron-nuclear wavefunction — ●ALI ABEDI¹, FEDERICA AGOSTINI¹, NEIPA MAITRA², and E. K. U. GROSS¹ — ¹Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, 06120 Halle, Germany — ²Department of Physics and Astronomy, Hunter College and the City University of New York, New York, New York 10065, USA

We present an exact factorization of the complete wavefunction into a purely nuclear part and an electronic wavefunction which parametrically depends on the nuclear configuration. We derive equations of motion for the nuclear and electronic wavefunctions. The nuclear dynamics is governed by a time-dependent Schrödinger equation featuring a vector potential and a potential energy surface. These potentials are unique and give a purely nuclear wave-function yielding the true nuclear N-body density and the true nuclear N-body current density of the full electron-nuclear system. Hence, in the classical limit, the gradient of this exact potential energy surface yields the "correct" classical force on the nuclei [3,4]. Therefore, the exact splitting of electronic and nuclear degrees of freedom lends itself as a rigorous starting point for the systematic development of (semi)classical approximations. Here, we present a novel mixed-quantum-classical algorithm to treat the coupled electron-nuclear motion. [1] A. Abedi, N.T. Maitra, E.K.U. Gross, PRL 105, 123002 (2010). [2] A. Abedi, N.T. Maitra, E.K.U. Gross, JCP 137, 22A530 (2012). [3] A. Abedi, F. Agostini, Y. Suzuki, E.K.U. Gross, PRL 110, 263001 (2013). [4] F. Agostini, A. Abedi, Y. Suzuki and E.K.U. Gross, Mol. Phys. 111, 3625 (2013)

MO 18.6 Thu 15:15 BEBEL SR144

Fixing long range behaviour: range separated functionals — ●ROLF WÜRDEMANN¹ and MICHAEL WALTER^{1,2} — ¹FMF, Uni-Freiburg, Freiburg, Germany — ²IWM, Freiburg, Germany

The description of exchange and correlation energies in density functional theory (DFT) in the local- or semi-local approximation is quite successful. But it also leads to an improper description of the effective potential in the $r \rightarrow \infty$ asymptote. This leads to an improper description of the interactions between s and d electrons in transition metals and problems including charge transfer.

Hartree-Fock theory (HFT) evaluates also non-local contributions to the exchange energy and is also referred as "exact exchange". By its definition HFT is free of delocalisation errors but suffers from the lack of the inclusion of (dynamic) correlation.

Range separating functionals (RSF) use a distance dependent function to switch between HFT and DFT dependent on the spatial distance between the two points under consideration. Thus it is possible to use DFT on short-range and HFT on long-range interaction, correcting the long-range behaviour of DFT. Functionals of this type are also called long-range corrected (LC) functionals. We discuss our implementation of LC using a multi grid technique and show first results.

MO 18.7 Thu 15:30 BEBEL SR144

Reflectance Anisotropy spectrum of water covered Cu(110) surface studied from first principles. — ●AMIRREZA BAGHBANPOURASL¹, KURT HINGERL¹, and WOLF GERO SCHMIDT² — ¹Johannes Kepler University Linz — ²University of Paderborn

In this contribution we study Reflectance Anisotropy Spectroscopy (RAS) of Cu(110) surface covered with different water structures. Reflectance Anisotropy Spectroscopy is a simple and useful optical surface sensitive probe which can be used to study water covered surfaces. Theoretical calculations that are necessary to aid preparing experimental setup and to interpret the results are not present in literature for water covered copper surface. For this purpose we used Density Functional Theory to calculate dielectric constant and then RAS of Cu(110) surface with the latest studied water adsorbed structures. At the end the effect of different adsorption structures on RAS and surface states is studied.

MO 19: Femtosecond Spectroscopy 2

Time: Thursday 16:30–18:15

Location: BEBEL HS213

MO 19.1 Thu 16:30 BEBEL HS213

Ultrafast emission quenching in perylene diimides by structure rearrangement induced electron transfer — ●PATRICK KÖLLE¹, IGOR PUGLIESI², ARTUR NENOV¹, HEINZ LANGHALS¹, EBERHARD RIEDLE², and REGINA DE VIVIE-RIEDLE¹ — ¹LMU München, Department Chemie, München, Germany — ²LMU München, LS BioMolekulare Optik, München, Germany

Perylene dyes have attracted great interest for the design of intramolecular energy and charge transfer systems. The influence of substitution of two fluorescent perylene diimides on the ultrafast intramolecular dynamics leading to efficient fluorescence quenching are investigated by transient spectroscopy and quantum chemical calculations. The fluorescent systems show no dynamics in the sub-nanosecond time region. For the first, the amino-functionalized molecule the stimulated emission signal decays rapidly on a sub-picosecond timescale, while the excited state absorption decreases with a time constant of several picoseconds. The theoretical analysis assigns the fast decay of the emission to a charge transfer from the amino substituent to the perylene diimide chromophore. Experiments and theoretical PCM calculations in different solvents demonstrate that the dynamics of this fluorescence quenching correlate with the solvation time. For the second, the phenyl-functionalized perylene diimide a similar charge transfer emission quenching mechanism is observed. An efficient and fast fluorescence quenching still occurs but in comparison with the amino-functionalized molecule the lifetime of the charge separation is increased by more than a factor of ten.

MO 19.2 Thu 16:45 BEBEL HS213

Quantum dynamical studies of diphenylmethylchloride including geometry relaxation and a three-state conical intersection seam — ●MATTHIAS K. ROOS, SEBASTIAN THALLMAIR, and REGINA DE VIVIE-RIEDLE — Department Chemie, Ludwig-Maximilians-Universität München

Reactive species like carbocations and -radicals are ubiquitous in organic synthesis. A convenient precursor for such intermediates is diphenylmethylchloride that is undergoing a carbon-chlorine bond cleavage after laser irradiation. We are using quantum chemical and quantum dynamical methods to evaluate the branching ratio between product pathways through consecutive conical intersections for this sub-picosecond ultrafast dissociation reaction. We present a new reduced coordinate space to describe the reaction using the Wilson G matrix approach for the kinetic Hamiltonian. With this method we can use combined internal coordinates that particularly account for all relaxation in the molecule during the dissociation process.

Resulting 1D and 2D potential energy surfaces on the ONIOM(CASSCF(12,10)/B3LYP) level of theory are presented and compared with respect to the approximation applied. Especially the influence of the chlorine lone pairs is discussed that have a significant impact on the dissociation dynamics through a prominent three-state conical intersection seam in the Franck-Condon region. The shape of the G matrix elements can be traced back to the relaxation included in the chosen coordinates. Dynamical results taking into account all relevant conical intersections are presented.

MO 19.3 Thu 17:00 BEBEL HS213

H-bond analysis of acetic acid by spontaneous and coherent Raman spectroscopy — ●MATTHIAS LÜTGENS, FRANK FRIEDRISZIK, SUSANA CHATZIPAPADOPOULOS, and STEFAN LOCHBRUNNER — Institut für Physik, Universität Rostock, 18055 Rostock

The formation of hydrogen bonds leads in many liquids to the appearance of molecular complexes and greatly affects their macroscopic properties. The structural motives of acetic acid (AA) are still under intense investigation, since AA has multiple H-bond donor and acceptor sites allowing for several configurations. The H-bonded complexes are investigated by comparing spontaneous Raman and coherent anti-Stokes Raman scattering (CARS) spectra of the C=O vibration. The spontaneous Raman spectrum shows three distinct features but cannot clearly decide if a fourth mode is contributing or not. CARS measurements with coherent excitation of the C=O band via a femtosecond Stokes and a narrowband Raman pump pulse followed by a narrowband probe pulse in the ps range can discriminate slow dephasing modes from faster dephasing vibrational contributions.[1] They reveal

an additional mode hidden under the dominating broad Raman band proving the coexistence of more than one H-bonded configuration in liquid AA.

[1] M. Lütgens, S. Chatzipapadopoulos, and S. Lochbrunner, *Opt. Express* 20, 6478-6487 (2012)

MO 19.4 Thu 17:15 BEBEL HS213

Excited-State Dynamics of the 2-Methylallyl Radical — ●JÖRG HERTERICH, THIEMO GERBICH, and INGO FISCHER — Institut für Physikalische und Theoretische Chemie, Universität Würzburg

The excited-state dynamics of hydrocarbon radicals is not well understood and only a few species have been studied. In many radicals, the electronically excited states are short-lived due to rapid internal conversion (IC). This fast deactivation can be used to prepare internally hot radicals for further studies of their unimolecular reactions. The excited-state dynamics of the 2-methylallyl radical are studied by time-resolved photoionization. The radical, which is relevant for combustion processes, is generated by pyrolysis from the corresponding bromide. The lifetime of the electronically excited B state was measured to be 14 ps and shorter.

MO 19.5 Thu 17:30 BEBEL HS213

Photodynamics and structure of a 1-methylthymine self-pair mediated by a silver trimer — ●YEVGENIY NOSENKO¹, CHRISTOPH RIEHN¹, GEREON NIEDNER-SCHATTEBURG¹, and WIM KLOPPER² — ¹TU Kaiserslautern, FB Chemie und Forschungszentrum OPTIMAS, Erwin-Schrödinger-Str. 52, 67663 Kaiserslautern — ²Karlsruher Institut für Technologie (KIT), Institut für Physikalische Chemie, Fritz-Haber-Weg 2, 76131 Karlsruhe

A cationic self-pair of deprotonated 1-methylthymine (1MT-H) mediated by a unique linear arrangement of three silver ions, [(Ag)₃(1MT-H)₂]⁺, was obtained by electrospray ionization from a methanolic solution and investigated in an ion trap at ca. 305 K by laser spectroscopy. Structure and photodynamics of the MBP was explored using IR multiple photon dissociation, femtosecond transient photo-fragmentation (PF) and ab initio calculations at the CC2 level of theory. Two time constants, 0.16(12) ps and 1.0(3) ps, are obtained from fitting of the 283 nm pump - 700 nm probe transient PF spectrum. The picosecond component is several times faster than in the thymine monomer, indicating an acceleration of the electronic relaxation induced by the metal coordination. Electronic relaxation pathways via LMCT or metal centered singlet excited states are discussed.

MO 19.6 Thu 17:45 BEBEL HS213

Pyrene: A textbook paradigm for excimer formation with some surprises — ●BASTIAN BAUDISCH, MARIO MASETTO, IGOR PUGLIESI, and EBERHARD RIEDLE — LS für BioMolekulare Optik, LMU München

Pyrene is the textbook example for excimers and their formation. It relies largely on nanosecond fluorescence measurements by Birks in the 60s [1]. After excitation 370-425 nm fluorescence occurs out of the S₁ state. Due to the long S₁ life time the excited pyrene molecules diffusively encounter ground state pyrenes and form excimers which give rise to red shifted fluorescence around 475 nm. We have investigated pyrene with extended pump-probe capabilities [2]. After 334 nm excitation into the S₂ state, we observe 85 fs relaxation to the S₁ state. In the subsequent dynamics an approximate doubling of the GSB in 6.6 ps occurs. In the ps and ns regime we observe clear signatures of anionic and cationic pyrene. Contrary to the commonly accepted mechanism our results indicate the presence of pre-associated dimers: After the optical excitation of one of the monomers a charge separation/transfer happens and leads to the bleaching of a second monomer. The resulting excited dimer then fluoresces and finally crosses into the triplet manifold. Observation of the dynamics is obscured by an intrinsic impurity identified by excitation wavelength dependent ns fluorescence decay dynamics. The impurity is found even for highly purified samples and seems to originate from a photochemical process.

[1] J. B. Birks et al., *Proc. Roy. Soc. A* **1963**, 275, 575.

[2] E. Riedle et al., *Faraday Discuss.* **2013**, 163, 139.

MO 19.7 Thu 18:00 BEBEL HS213

Impact of Different Hydrogen Bond Sites on the Molecu-

lar Network of Ionic Liquids from Ultrafast CARS Spectroscopy — ●SUSANA CHATZIPAPADOPOULOS¹, MATTHIAS LÜTGENS¹, FRANK FRIEDRISZIK¹, TOBIAS ZENTEL¹, DANIELA KERLÉ², OLIVER KÜHN¹, RALF LUDWIG², and STEFAN LOCHBRUNNER¹ — ¹Institut für Physik, Universität Rostock, Germany — ²Institut für Chemie, Universität Rostock, Germany

Ionic liquids (ILs) have unique properties which depend critically on the interaction between the ions. Understanding the intermolecular forces might enable an application-oriented tuning of their macroscopic properties. Here we study different imidazolium based ILs of the type [TeMIM][NTf₂] with femtosecond multiplex CARS. Dephasing times and vibrational resonance frequencies are extracted by quantitative

modeling of the complete CARS response. In previous investigations on a similar system of the type [C_nMIM][NTf₂] we found a hydrogen bond network formed by the three hydrogen atoms of the imidazolium ring [1]. In the present study we modified the ILs and replaced two hydrogens by methyl groups. In this way a simplified network with only one hydrogen bond per cation results and the bond position can be varied. From the frequencies of the isolated resonances an unambiguous assignment of the hydrogen bonds in the complete network with three hydrogen donors per cation is established. Spectral shifts and changes in dephasing times are discussed with respect to differences between the complete and the simplified hydrogen bond network.

[1] C. Roth et al., *New J. Physics* **14** (2012), 105026.

MO 20: Electronic Spectroscopy 2

Time: Thursday 16:30–18:30

Location: BEBEL SR144

MO 20.1 Thu 16:30 BEBEL SR144

Electronic Spectroscopy of 1-Phenylethynyl-Naphthalene — ●PHILIPP CONSTANTINIDIS¹, MELANIE LANG¹, JÖRG HERTERICH¹, INGO FISCHER¹, JOHANNES AUERSWALD², and ANKE KRUEGER² — ¹Institute of Physical and Theoretical Chemistry, University of Würzburg, Am Hubland, D-97074 Würzburg, Germany — ²Institute of Organic Chemistry, University of Würzburg, Am Hubland, D-97074 Würzburg, Germany

A recent IR/UV double resonance study identified 1-phenylethynyl-naphthalene (1-PEN) as the major dimerization product of phenyl-propargyl radicals. Considering the importance of C₃ hydrocarbons in the initial phase of the formation of polycyclic aromatic hydrocarbons (PAHs) in combustion processes, both the phenylpropargyl radical as C₉ unit and its stable dimer 1-PEN could also play a conceivable role in PAH growth [1].

We investigated the S₁ excited state of 1-PEN by means of [1+1]-REMPI spectroscopy. A rich structure of low wavenumber bands was observed, which could be assigned to the torsional motion. Vibrational frequencies of 6 cm⁻¹ and 17 cm⁻¹ respectively were derived for the torsional mode in the ground and excited state. Spectra of the 1-PEN/Ar cluster exhibit a red shift of the origin of 22 cm⁻¹, comparable to argon clusters of other aromatic molecules.

[1] K. H. Fischer, J. Herterich, I. Fischer, S. Jaecx and A. M. Rijs, *J. Phys. Chem. A* **116**, 8515 (2012)

MO 20.2 Thu 16:45 BEBEL SR144

The Hydrogen Bond of Water in Mixtures with Organic Solvents and in Aqueous Ion Solutions — ●KATHRIN MARIA LANGE, TRISTAN PETIT, GERRIT CONRAD, KENJI YAMAMOTO, CHRISTOPH SCHWANKE, KAI HODECK, MARKUS DANTZ, TIM BRANDENBURG, EDLIRA SULJOTI, and EMAD FLEAR AZIZ — Helmholtz-Zentrum Berlin, Germany

Knowledge about the hydrogen bond network of water is essential for understanding its anomalies as well as its special role for several biochemical systems. Soft X-ray absorption (XAS) and emission spectroscopy (XES) as well as resonant inelastic X-ray scattering (RIXS) at the oxygen K-edge of water allow investigating its local electronic structure by probing the occupied- and unoccupied-valence molecular orbitals. The recent combination of these methods with the liquid microjet technique opened the door to studies of the hydrogen bond nature in a membrane-free spectrometer.[1-4] The effect of confining water in organic solvents free from oxygen[2], replacing hydrogen by deuterium [3] as well as of dissolving monovalent cations (Li⁺, K⁺, NH₄⁺, Na⁺) [4] on the hydrogen bond structure of water was characterized. For the ionic solutions cation ordering with respect to their impact on hydrogen bond network was revealed and the effect of the counterion was investigated. [1] Lange et al., *Chemical Physics* **377**, 1-5 (2010) [2] Lange et al., *Angewandte Chemie* **123**, 45, 10809 (2011) [3] Lange et al., *Phys. Rev. B* **85**, 155104 (2012) [4] Petit, Lange, Conrad, Yamamoto, Schwanke, Hodeck, Dantz, Brandenburg, Suljoti, Aziz, Submitted 2013

MO 20.3 Thu 17:00 BEBEL SR144

Determination of Excited State Dipole Moments from Electronic Stark Measurements — ●MICHAEL SCHMITT¹, JOSEFIN ROLF¹, MARTIN WILKE¹, and W. LEO MEERTS² — ¹Heinrich-Heine-

Universität Düsseldorf, Institut für Physikalische Chemie, Düsseldorf, Deutschland — ²Radboud University, Molecular and Biophysics group, Nijmegen, The Netherlands

The dipole moments of electronically excited states may differ considerably from those of the ground state, as a consequence of the altered electron distribution upon excitation. This change of the dipole moment upon electronic excitation has a large influence on solvation dynamics, which is largely governed by the interactions of solute and solvent dipole moments.

We modified the existing setup for rotationally resolved electronic spectroscopy by inserting a pair of Stark plates in the laser-molecular beam interaction region. They consist of a parallel pair of electroformed nickel wire mesh (70 mesh per inch) with a transmission of 95% in the UV. The polarization plane of the incoming laser beam can be rotated by 90° inside the vacuum chamber by means of an achromatic λ/2 plate. For the polarization being parallel to the electric field of the Stark plates ΔM = 0 and for the polarization being perpendicular to the electric field ΔM = ±1 selection rules apply.

The spectra of several indole derivatives have been fit automatically using an evolutionary strategy. The nature of the excited states is discussed, using the informations from the excited state dipole moments.

MO 20.4 Thu 17:15 BEBEL SR144

Ultrafast dynamics of solvated electrons in NaI aqueous solution — ●ALEXANDER KOTHE, NICHOLAS ENGEL, ALEXANDRE MOGULEVSKI, MARTIN WILKE, IGOR YU. KIYAN, and EMAD F. AZIZ — Joint Ultrafast Dynamics Lab in Solutions and at Interfaces (JULiq), Helmholtz-Zentrum Berlin für Materialien und Energie (HZB), Albert-Einstein-Str. 15, 12489 Berlin, and Freie Universität Berlin, FB Physik, Arnimallee 14, 14195 Berlin, Germany

Due to the importance of water in physics, chemistry and biology the solvated electron has drawn a lot of scientific interest since its discovery [1]. In our pump-probe experiment we generated solvated electrons in a liquid microjet with 20 mM NaI aqueous solution using laser pulses with a wavelength of 266 nm. The system was probed via photoemission spectroscopy with pulses of 350 nm wavelength. We observed the so called "hot" solvated electrons [2] and an additional excited state with a binding energy of 1.6 eV and a lifetime of approximately 4 ps.

Furthermore, rotating the pump beam and thus orienting the excited state with respect to the probe beam and the spectrometer axis revealed polarization dependence of the "hot" solvated electrons. In contrast to this finding, the excited state with the binding energy of 1.6 eV did not depend on its orientation.

[1] E. J. Hart and J. W. Boag, *J. Am. Chem. Soc.* **84**, 4090 (1962).

[2] A. Lübcke, F. Buchner, N. Heine, I. V. Hertel and T. Schultz, *Phys. Chem. Chem. Phys.* **12**, 14629 (2010).

MO 20.5 Thu 17:30 BEBEL SR144

Chemical Bonding in Aqueous Ferrocyanide: Experimental and Theoretical X-ray Spectroscopic Study — ●NICHOLAS ENGEL¹, SERGEY I. BOKAREV², EDLIRA SULJOTI¹, RAUL GARCIA-DIEZ¹, KATHIN M. LANGE¹, KAAAN ATAK¹, RONNY GOLNAK¹, ALEXANDER KOTHE¹, MARCUS DANTZ¹, OLIVER KÜHN², and EMAD F. AZIZ¹ — ¹Joint Ultrafast Dynamics Lab in Solutions and at Interfaces at Helmholtz-Zentrum Berlin für Materialien und Energie, Albert-Einstein-Straße 14, 12489 Berlin and Freie Universität Berlin, Department of Physics, Arnimallee 14, 14195 Berlin — ²Institut für Physik,

Universität Rostock, Universitätsplatz 3, 18055 Rostock

Exploiting the recently developed micro-jet technique enables to investigate liquid phase samples with the use of soft X-ray spectroscopy. Here, resonant inelastic X-ray scattering (RIXS) and X-ray absorption (XA) experiments at the iron L- and nitrogen K-edge are combined with high-level first principles restricted active space self-consistent field (RASSCF) calculations for a systematic investigation of the nature of the chemical bond in potassium ferrocyanide in aqueous solution. The atom- and site-specific RIXS excitations and the high resolution of the beamline and spectrometer <0.5 eV allow for direct observation of ligand-to-metal (Fe L-edge) and metal-to-ligand (N K-edge) charge transfer bands and thereby evidence for strong σ -donation and π -back-donation. The effects are identified by comparing experimental and simulated spectra related to both the unoccupied and occupied molecular orbitals in solution.

MO 20.6 Thu 17:45 BEBEL SR144

Triplet-triplet exciton dynamics in single-wall carbon nanotubes — ●FLORIAN SPÄTH¹, DOMINIK STICH¹, HANNES KRAUS², ANDREAS SPERLICH², VLADIMIR DYAKONOV^{2,3}, and TOBIAS HERTEL¹ — ¹Institute of Physical and Theoretical Chemistry, Julius-Maximilian University Würzburg, Germany — ²Institute of Physics, Julius-Maximilian University Würzburg, Germany — ³Bavarian Center for Applied Energy Research e.V., Würzburg, Germany

Understanding triplet excitons dynamics is crucial for the optimization of optoelectronic devices, since triplet excitons can either increase the efficiency of devices such as OLEDs and organic solar cells or can act as a loss channel. For the first time, triplet-triplet exciton interactions in (6,5)-single-wall carbon nanotubes (SWNTs) were studied by optically detected magnetic resonance (ODMR) spectroscopy[1]. By using a master equation ansatz and taking into account the excitation intensity and frequency dependence of the ODMR signal, we were able to determine the quantum yield of triplet exciton formation of (5 ± 2)% and the triplet exciton lifetime of (30 ± 10) μ s.

[1] D. Stich, F. Späth, H. Kraus, A. Sperlich, V. Dyakonov and T. Hertel, *Nature Photonics*, in press (doi: 10.1038/nphoton.2013.316)

MO 20.7 Thu 18:00 BEBEL SR144

From 5 to 6: High resolution laser induced fluorescence spectroscopy of differently substituted indole derivatives. — ●MARTIN WILKE, JOSEFIN ROLF, and MICHAEL SCHMITT — Heinrich-Heine-Universität, Institut für Physikalische Chemie I, Düsseldorf

The assignment of the electronic nature of several 6-substituted indole derivatives with high resolution laser induced fluorescence spectroscopy will be presented. Its characterization to an La or an Lb state based on the orientation of the transition dipole moment, the changes of the bond lengths or the frontier orbital contribution upon excitation. Comparing the experimental results with state-of-the-art ab initio calculations shows a strong discrepancy in the orientation of the transition dipole moment from the results for the 5-substituted indoles. The surprising behavior of the 6-substituted derivatives compared to the 5-substituted derivatives will be discussed.

MO 20.8 Thu 18:15 BEBEL SR144

A new experimental set-up for electronic Stark measurements with rotationally resolved laser induced fluorescence spectroscopy — ●JOSEFIN ROLF, MARTIN WILKE, and MICHAEL SCHMITT — Heinrich-Heine-Universität, Institut für Physikalische Chemie I, Düsseldorf

High resolution laser induced fluorescence spectroscopy can be used to assign the electronic nature of excited singlet states. Therefore, several molecular parameters like the orientation of the transition dipole moment, the changes of the bond lengths or the frontier orbital contribution upon excitation are needed to determine the electronic nature. It is also possible to get the permanent electric dipole moment of the ground and the excited state by changing the experimental set-up. These realized technical changes to generate a homogeneous electric field and to modify the polarisation of the laser beam will be presented. The electric field 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. By switching the polarization of the laser between horizontal and vertical different selection rules will be applied.

MO 21: Photochemistry

Time: Friday 10:30–12:30

Location: BEBEL HS213

MO 21.1 Fri 10:30 BEBEL HS213

The Photodissociation Dynamics of Fulvenallene, C₇H₆, Investigated by Velocity Map Imaging — ●JENS GIEGERICH and INGO FISCHER — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland Süd, Würzburg

Fulvenallene is the most stable C₇H₆ isomer and is assumed to be an intermediate in the combustion of toluene. C₇H₆ has been observed in toluene rich flames and theoretical studies predict it to be the major decomposition product of the benzyl radical. It appears that fulvenallene is an important intermediate in oxidation and pyrolysis processes, which are relevant to the combustion of aromatic hydrocarbons and to the formation of PAH.

Fulvenallene was generated from phthalide as a precursor, which decomposes to the reactive intermediate in a vacuum jet flash pyrolysis source. The molecules were excited at around 247 nm. At this wavelength region the excited molecule dissociates to the fulvenallenyl radical C₇H₅ + H. The H-atom dissociation products were ionized in a [1+1] REMPI process via the 1s-2p transition. The ionized H-atoms are recorded on a Velocity Map Imaging Detector. The observed translational energy distribution peaks around 0.06 eV. The expectation value for translational energy release lies at around 0.21 eV which accords to $\sim 14\%$ of the excess energy. The ionized H-atoms show an isotropic angular distribution, typical for statistical reactions. In addition time-delay scans were carried out. The time-delay scans show a rate with a time constant on the order of 150 ns and are in good agreement with RRKM predictions.

MO 21.2 Fri 10:45 BEBEL HS213

Solvent Dependence of Excited-State Proton Transfer from Pyranine-derived Photoacids — ●CHRISTIAN SPIES¹, BJÖRN FINKLER¹, DINA PINES², EHUD PINES², DAN HUPPERT³, and GREGOR JUNG¹ — ¹Biophysical Chemistry, Saarland University, Saarbrücken,

Germany — ²Department of Chemistry, Ben-Gurion University of the Negev, Beer-Sheva, Israel — ³Raymond and Beverly Sackler Faculty of Exact Sciences, School of Chemistry, Tel Aviv University, Israel

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 hydroxypyrenyl-trisulfonate (HPTS) and its even more acidic sulfonamide derivative (HPTA). Recently, we synthesized a new series of strong photoacids based on HPTS and HPTA, with high photostability and pK_a* values ranging from -0.7 to -4. In this contribution we study the solvent dependence of these photoacids. A differential solvatochromism approach enables us to identify a charge transfer as the most distinct feature for the strong solvatochromism and photoacidity of these molecules. The excited-state proton transfer rate (kPT) of these photoacids is measured in more detail by time-resolved spectroscopy. Different solvents in which proton transfer takes place such as water, methanol and ethanol are investigated. The results are quantitatively explained by adiabatic and non-adiabatic proton transfer formalism and analyzed in terms of Marcus free energy correlations.

MO 21.3 Fri 11:00 BEBEL HS213

Self-Assembly and Size-Dependent Optical Properties of Perylene Bisimide Dye Aggregates — ●FRANZISKA FENNEL¹, STEFFEN WOLTER¹, ZENGQI XIE², PER-ARNO PLÖTZ¹, OLIVER KÜHN¹, FRANK WÜRTHNER², and STEFAN LOCHBRUNNER¹ — ¹Institut für Physik, Universität Rostock, Universitätsplatz 3, 18055 Rostock — ²Institut für Organische Chemie und Center for Nanosystem Chemistry, Universität Würzburg, Am Hubland, 97074 Würzburg

Molecular self-assembly is widely applied to create functional nanostructures. However, in many cases a quantitative description of the

assembly processes is missing. In the presented work, the self-assembly of a perylene bisimide dye and the associated changes in the photophysical properties are investigated [1]. We find a remarkable behavior of the fluorescence yield upon aggregation, which first decreases and then increases again. The findings point to the presence of three different species during the assembly process, namely monomers, dimers with H-type and aggregates with J-type characteristics. An aggregation model is developed, which describes quantitatively the assembly process and the concentration dependence of the photophysical properties. The basic concept is that with increasing concentration first energetically favored dimers are formed which are not suitable for the association of further monomers due to their geometry. Larger aggregates are formed via a second dimeric species, which exhibits a different structure than the energetically favored dimer. This mechanism should also be responsible for the aggregation behavior of many other compounds. [1] Fennel F. et. al. *J. Am. Chem. Soc.*, **2013**, 135 (50),18722

MO 21.4 Fri 11:15 BEBEL HS213

Electron and Energy Transfer Processes in Homogeneous Photocatalytic Systems — ●ANTJE NEUBAUER¹, SERGEY I. BOKAREV², GILBERT GRELL², ALEKSEJ FRIEDRICH¹, PATRICK SCHWARZBACH¹, DAVID SCHALLENBERG³, WOLFRAM W. SEIDEL³, HENRIK JUNGE⁴, MATTHIAS BELLER⁴, OLIVER KÜHN², and STEFAN LOCHBRUNNER¹ — ¹Institut für Physik, Universität Rostock — ²Institut für Physik, Universität Rostock — ³Institut für Chemie, Universität Rostock — ⁴Leibniz-Institut für Katalyse Rostock

Photocatalytic water splitting for hydrogen generation has recently gained high scientific attention. However, there are only a few studies that focus on mechanistic insight on a molecular level.

Here we investigate homogeneous photocatalytic systems for water reduction based on Iridium(III)-photosensitizers (IrPS) with the aim to clarify the mechanisms of the individual reaction pathways relevant for photocatalysis. By employing time-resolved photoluminescence spectroscopy as well as time-dependent density functional theory calculations we address the following reaction steps: i) electron transfer from a sacrificial donor to the excited IrPS, and ii) excited state quenching of IrPS by an iron catalyst.

In addition to the unbound multi-component system, we study the intramolecular processes of a dinuclear Iridium-Nickel-complex with a novel phenanthroline-5,6-dithiolate bridging ligand. Such complexes have the potential of fast electron or energy transfer as essential reaction step in photophysical applications. For both systems, the role of electron and energy transfer processes is highlighted.

MO 21.5 Fri 11:30 BEBEL HS213

Proton Transfer in Aqueous Solutions — ●ISAAK UNGER¹, STEPHAN THÜRMER², and BERND WINTER¹ — ¹Helmholtz-Zentrum Berlin für Materialien und Energie — ²Center for Frontier Science, Chiba University, Japan

Synchrotron radiation has been used to core-excite several hydrogen-bonded species (Ammonia, Glycine) in aqueous solution using a liquid microjet as a sample. In contrast to gaseous samples, Auger decay is not the sole possible deexcitation channel in aqueous solutions. In the intermolecular Coulombic decay, the released energy upon a recombination of a valence electron with a core hole is transferred to a neighboring molecule releasing an electron. Auger electron spectroscopy of different aqueous solutions and their deuterated equivalents show a considerable influence of the proton mass on the decay probability of such delocalized deexcitation processes. We propose a model of proton transfer assisted decay to explain the different decay behaviour of deuterated species in hydrogen-bonded systems.

MO 21.6 Fri 11:45 BEBEL HS213

Structural investigations on the jet-cooled neutral and ionic 7-hydroxy-4-methylcoumarin dimer and its hydrates by combined IR/UV spectroscopy — ANKE STAMM, ●KIRSTEN SCHWING,

and MARKUS GERHARDS — Physikalische Chemie, TU Kaiserslautern, Erwin-Schrödinger-Straße 52, 67663 Kaiserslautern

The photochemistry of solvated 7-hydroxy-4-methylcoumarin (7H4MC), e.g. known as one of the first industrially applied optical brighteners, was intensively investigated in the past e.g. comprising absorption spectroscopy, fluorescence measurements leading to quantum yields and life times or phosphorescence and triplet-triplet spectra. In this context the influence of solvents on the photochemical behavior was one of the main interests. From aqueous solution it is additionally known that the coumarin dyes show a tendency for self-aggregation. However, no detailed experimental analysis of the intrinsic structural properties of 7H4MC was performed so far. Thus we applied mass-, (isomer-) and state-selective combined double and triple resonance IR/UV methods for 7-hydroxy-4-methylcoumarin. IR spectra of the neutral and ionic dimer (S_0 , D_0 states) of 7H4MC as well as its mono- and dihydrate could be obtained. A comparison with calculated IR spectra for possible DFT-optimized isomers of a species allowed structural assignments. The presented measurements on 7H4MC are the first gas phase investigations on a neutral and ionic dimer of a coumarin derivative. The tendency of coumarin dyes for self-aggregation observed in aqueous solution is now investigated in detail on isolated species which can be successively hydrated.

MO 21.7 Fri 12:00 BEBEL HS213

Quantumchemical studies on the decay of photoexcited 4,4'-Dihydroxythioindigo and its methylated counterpart — ●SVEN OESTERLING¹, MARC DITTMANN², FRANZISKA F. GRAUPNER³, BENJAMIN MAERZ³, WOLFGANG ZINTH³, MARTIN ENGELHARD², WOLFGANG LÜTTKE⁴, and REGINA DE VIVIE-RIEDLE¹ — ¹LMU München, Dept. Chemie, München, Germany — ²MPI für Molekulare Physiologie, Dortmund, Germany — ³LMU München, Fakultät für Physik, München, Germany — ⁴GAU Göttingen, Fakultät für Chemie, Göttingen, Germany

The Thioindigo derivatives 4,4'-Dihydroxythioindigo (DHTI) and 4,4'-Dimethoxythioindigo (DMTI) show different behaviour after photoexcitation. Both exhibit strong fluorescence, but the lifetime of the excited state of DHTI (50 ps) is roughly 200 times shorter than the one of DMTI (11 ns). Contrary to DHTI, in DMTI a *cis-trans*-isomerization around the central double bond can be observed, which stems from a deactivation pathway, known for thioindigo itself, too.

Our quantumchemical calculations on CASSCF/PT2 level of theory reveal a different route to reach the ground state for DHTI, mediated through an excited state intramolecular proton transfer (ESIPT). Although the corresponding conical intersection lies below the Franck-Condon energy in DMTI, too, this path is obstructed for DMTI, where, instead of a proton, a methylation had to be transferred.

Marc Dittmann et al., *Angew. Ch. Int. Ed.* **2013**, 52, 1-5

MO 21.8 Fri 12:15 BEBEL HS213

A coherent-control study of 6-nitro BIPS — ●CRISTINA CONSANI, STEFAN RUETZEL, PATRICK NUERNBERGER, and TOBIAS BRIXNER — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

We present a coherent-control study on the isomerizing merocyanine dye 6-nitro BIPS in liquid environment. This molecule has been extensively studied in our group by means of ultrafast transient absorption and two-dimensional (2D) electronic spectroscopy, unraveling the details of the photo-induced isomerization. Two-dimensional spectroscopy represents an example of how extended photochemical information can be retrieved by employing a modulated electric field as excitation pulse. Coherent control techniques are a natural extension of this concept. In our approach, the results of 2D spectroscopy are used as input for the control study. We investigate how systematic variation of the excitation field within restricted parametrization spaces can be used to address specific molecular processes, thus completing and extending the information obtained by third-order spectroscopies.

MO 22: Cold Molecules 3

Time: Friday 10:30–12:00

Location: BEBEL SR144

MO 22.1 Fri 10:30 BEBEL SR144

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 Aimé 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 cm⁻¹ 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 22.2 Fri 10:45 BEBEL SR144

Ne* + NH₃: Polyatomic Chemical Reactions in the Low-Temperature Regime — ●JUSTIN JANKUNAS, BENJAMIN BERTSCHE, and ANDREAS OSTERWALDER — Ecole Polytechnique Federale de Lausanne

A novel merged beam (MB) technique for neutral molecules has been employed to study bimolecular collisions between electronically excited neon atoms and supersonically cooled ammonia molecules. Cross sections of the two reaction channels, namely Ne* + NH₃ → Ne + NH₃⁺ + e- and Ne* + NH₃ → Ne + NH₂⁺ + H + e-, have been measured as a function of relative velocity between Ne* and NH₃. The lowest and highest collision energies achieved are 0.1 K (8 μeV) and 250 K (0.22 meV), respectively. We find that the cross section for the two reaction channels increases upon lowering the collision energy. The long range forces dominate the outcome of a reaction in the 0.1 K to ~ 10 K temperature range. The role played by short-ranged chemical forces becomes apparent when the collision energy is greater than ~ 10 K. We have also measured the ratio, Γ = NH₂⁺ / (NH₂⁺ + NH₃⁺), of the two reaction channels. Surprisingly, the ratio is constant (Γ ~ 0.3) in the collision energy range studied, defying our naïve expectation that as the collision energy vanishes, a channel with a lower minimum energy path dominates the reaction. We suggest that similar effects may be present in other electron transfer reactions.

MO 22.3 Fri 11:00 BEBEL SR144

Ultracold collisions of a³Σ_u⁺ molecules — ●BJÖRN DREWS, MARKUS DEISS, BENJAMIN DESSLER, and JOHANNES HECKER DEN-SCHLAG — Institut für Quantenmaterie, Universität Ulm

We prepare a sample of ultracold ⁸⁷Rb₂ molecules in the a³Σ_u rovibrational ground state in a three dimensional optical lattice. Starting from there we allow interaction in one (cigar-shaped trap) or two (pancake trap) directions. Fast inelastic two-body-collision losses are expected due to the energetically lower-lying x¹Σ_g potential. The observed lifetimes are on timescales ranging from a few up to hundreds of milliseconds and we see a dependency on the trap depth and on the external magnetic field.

With the ability to change the internal state of the molecule as well as the surrounding fields these experiments present a testing ground for ultracold chemistry. Data over a wide range of different experimental parameters will be shown as well as their placement in a theoretical background.

MO 22.4 Fri 11:15 BEBEL SR144

Non-adiabatic alignment of molecules dissolved in small helium clusters — G. GALINIS¹, L.G. MENDOZA LUNA¹, M. WATKINS¹,

●K. VON HAEFTEN¹, R. MINNS², A.M. ELLIS³, R. CHAPMAN⁴, C. CACHO⁴, E. TURCU⁴, E. SPRINGATE⁴, M. MLADENOVICH⁵, M. LEWERENZ⁵, L. KAZAK⁶, R. IRSIG⁶, S. SKRUSZEWICZ⁶, S. GÖDE⁶, J. TIGGESBÄUMKER⁶, K.H. MEIWES-BROER⁶, A. ROUZEE⁷, and R. ZILLICH⁸ — ¹Dep. of Physics and Astronomy, University of Leicester, UK — ²Dep. of Chemistry, University of Southampton, UK — ³Dep. of Chemistry, University of Leicester, UK — ⁴Central Laser Facility, Rutherford Appleton Lab, UK — ⁵Laboratoire Modelisation et Simulation, University of Paris-Est, Marne-la-Valee, France — ⁶Institute for Physics, University of Rostock, Germany — ⁷Max Born Institute, Berlin, Germany — ⁸Institute for Theoretical Physics, University Linz, Austria

The rotational dynamics of C₂H₂ molecules in small helium clusters was investigated using laser induced alignment in a pump-probe experiment. The Fourier-transform of the time-trace shows sharp, cluster-specific spectral features with coherence times limited only by our experimental resolution, contrary to the findings for molecules in helium droplets¹. The generation of highly charged atomic and molecular ions, the formation and propagation of rotational and vibrational wavepackets, the role of cluster size and the relevance of this work in the study of incipient superfluid effects in small helium clusters will be discussed.

¹ D. Pentlehner et al., Phys. Rev. Lett. **110**, 093002 (2013)

MO 22.5 Fri 11:30 BEBEL SR144

IR spectroscopy of biomolecular ions in liquid helium droplets — ●DOO-SIK AHN, ANA ISABEL GONZALEZ FLORENZ, and GERT VON HELDEN — Fritz-Haber-Institut, Berlin, Germany

Liquid helium droplets are ideal nano-cryostats for the investigation of molecules because of intrinsic characters of superfluid helium droplets such as isothermality at 0.38 K, the weak interaction between the helium matrix and dopant, and a transparency over a wide spectral range from the far IR to the deep UV. For the application of this technique to the cooling and spectroscopic investigation of biomolecular ions in the gas phase, we have developed an experimental setup where mass/charge selected biomolecular ions picked up by helium droplets. The size-distributions of ion-doped He droplets are analyzed by the measurement of arrival time distributions at different acceleration field. IR Spectroscopy can be performed by irradiating the ion-doped He droplets with a pulsed laser and monitoring ejected ions as a function of wavelength. In this talk, we will report very recent result of IR spectroscopy of various peptide ions doped in He droplets using FHI(Fritz-Haber-Institut) free electron laser.

MO 22.6 Fri 11:45 BEBEL SR144

Rydberg states of alkali atoms on helium nanodroplets: Screening effects of a nanosized helium dielectric — FLORIAN LACKNER, GÜNTER KROIS, and ●WOLFGANG E. ERNST — Institute of Experimental Physics, Graz University of Technology, Graz, Austria

Rydberg series of Rb and Cs atoms on the surface of helium nanodroplets (HeN) [1] have been studied by resonance enhanced multiphoton ionization and laser induced fluorescence spectroscopy. The recorded excitation spectra [2,3] are analyzed by using a Rydberg-Ritz approach [4]. The dependence of the quantum defects on the principal quantum number within a Rydberg series gives insight into the interaction between the alkali valence electron and the superfluid helium droplet. For higher excited states, a screening of the valence electron from the alkali atom core by the helium droplet is observed, i.e. the helium reduces the probability to find the high-n electron nearby the core [4]. For lower states, the screening effect decreases and the quantum defects are found to lie closer to free atom values. In addition, the large spin-orbit constant of the Cs-HeN P states allows a detailed study of the influence of the helium droplet on the SO splitting as function of the principal quantum number. [1] C. Callegari and W.E. Ernst, in Handbook of High-Resolution Spectroscopy, edited by M. Quack and F. Merkt (John Wiley & Sons, Chichester, 2011), Vol. 3, pp. 1551-1594 [2] F. Lackner, G. Krois, M. Theisen, M. Koch, and W. E. Ernst, Phys. Chem. Chem. Phys. 2011, 13, 18781 [3] F. Lackner, G. Krois, M. Koch, and W. E. Ernst, J. Phys. Chem. Lett. 2012, 3, 1404 [4] F. Lackner, G. Krois, and W. E. Ernst, Mol. Phys. 2013, 111, 2118

MO 23: Femtosecond Spectroscopy 3

Time: Friday 14:00–15:45

Location: BEBEL HS213

MO 23.1 Fri 14:00 BEBEL HS213

Transient grating spectroscopy with extreme ultraviolet light

— E. F. SISTRUNK¹, J. GRILJ^{1,2}, J. JEONG³, M. SAMANT³, A. X. GRAY⁴, H. A. DUERR⁴, M. KOCH⁵, S. S. P. PARKIN³, and ●M. GUEHR¹ — ¹PULSE, SLAC, Menlo Park, CA 94305, USA — ²EPFL Lausanne, CH-1015, Switzerland — ³IBM Almaden Research Center, San Jose, CA 95120, US — ⁴SIMES, SLAC, Menlo Park, CA 94305, USA — ⁵Experimental Physics, TU Graz, A-8010 Graz, Austria

Transient grating spectroscopy, introduced in the optical domain for its high signal-to-noise ratio at ultrafast time-resolution, has been a successful method for studying electronic and nuclear dynamics in molecules and solids. We demonstrate the first transient grating probed by ultrashort extreme ultraviolet pulses. The extreme ultraviolet range with photon energies from 10 to 100 eV provides element sensitivity on the important 3d transition elements via their 3p-3d core-to-valence resonances. We create a transient grating on VO₂, which undergoes an insulator-to-metal transition (IMT) upon optical excitation with 800 nm pulses. The probe pulse is generated by strong field high harmonic generation (HHG) and contains photon energies at the vanadium 3p-3d transition. It probes the transient grating in a reflective geometry under grazing incidence. The first diffraction order of the transient grating shows spectrally resolved harmonics of the probe pulse. The diffraction intensity rises with a several picosecond time constant followed by a decay over >100 ps. In the talk we will discuss the different mechanisms of diffraction from the VO₂ sample and the sensitivity to electronic and nuclear rearrangements in the IMT.

MO 23.2 Fri 14:15 BEBEL HS213

Strong field ionization of Butadiene with sub-7fs laser pulses

— ●SASCHA BIRKNER, FEDERICO FURCH, ALEXANDRIA ANDERSON, MARTIN GALBRAITH, JOCHEN MIKOSCH, CLAUS PETER SCHULZ, and MARC J.J. VRAKING — Max-Born-Institut, Berlin, Deutschland

Strong field ionization (SFI) is a sub-cycle spectroscopic method and underlies most other attosecond spectroscopies. In recent years, it has been shown that in polyatomic molecules not only the ionic ground state but also excited ionic states are populated during SFI [1,2,3]. By combing a high repetition 400 kHz laser system delivering sub-7 fs, 4 μJ pulses at 800 nm with a reaction microscope enabling coincident detection of ion and electron momentum, the SFI of 1,3-Butadiene has been investigated. For different ionic fragment groups distinct electron momentum distributions have been observed. Our studies are particularly sensitive to the kinetic energy release of the ionic fragments. First observations point towards statistically driven unimolecular decay of the electronically excited cation.

[1] H. Akagi, et al., Science 325, 1364 (2009).

[2] A.E. Boguslavskiy, et al., Science 335, 1336 (2012).

[3] J. Mikosch, et al., Phys. Rev. Lett. 110, 023004 (2013).

MO 23.3 Fri 14:30 BEBEL HS213

Individual surrounding effects – how a single counterion changes the photochemistry of phosphonium ions

— ●SEBASTIAN THALLMAIR^{1,2}, CHRISTIAN F. SAILER², EBERHARD RIEDLE², and REGINA DE VIVIE-RIEDLE¹ — ¹Department Chemie, LMU München — ²LS Für BioMolekulare Optik, LMU München

Photochemical bond cleavage of phosphonium ion is a common tool to generate carbocations in polar and moderately polar solvents. The degree of ion pairing – hence the distance to the counterion – as well as the type of counterion influence the product formation after the bond cleavage. Ultrafast transient absorption measurements have shown, that complex counterions like SbF₆⁻ or BF₄⁻ lead to the generation of carbocations while excitation of phosphonium salts with halides (e.g. Cl⁻, Br⁻) is followed by radical formation.

First we show the influence of the different counterions on the electronic excitations at the Franck-Condon point. Whereas the anions with a high oxidation potential (e.g. SbF₆⁻, BF₄⁻) do not contribute to the lowest excited singlet states while Cl⁻ or Br⁻ reveal another behaviour. These halides are relatively easily oxidized which can be seen in their contribution to the excited states manifold via charge transfer excitations.

On the basis of these results different reaction pathways depending on the counterion are presented. Our theoretical investigations clarify that besides the design of the phosphonium precursor and the chosen

solvent the counterion is an additional control knob for the photochemical bond cleavage of phosphonium salts.

MO 23.4 Fri 14:45 BEBEL HS213

Photo induced electron transfer in a self formed aluminum corrole - viologen complex.

— ●TILL STENSITZKI¹, ANGELICA ZACARIAS², ZEEVE GROSS³, ATIF MAHAMMED³, YANG YANG¹, and KARSTEN HEYNE¹ — ¹Department of Physics, Freie Universitaet Berlin, Berlin, Germany — ²Max-Planck-Institut fuer Mikrostrukturphysik und European Theoretical Spectroscopy Facility (ETSF), Germany — ³Schulich Faculty of Chemistry, Technion-Israel Institute of Technology, Haifa, Israel

Corroles are closed tetrapyrroles similar to porphyrines, missing a C-atom at a meso position. Like porphyrines, they serve as a ligand for different metals. Furthermore, their photo-reaction is quite complex, violating Kasha's rule and showing complex and not fully understood excited state absorption.

Using polarization resolved femtosecond transient absorption and other spectroscopic methods, we show that sulfonated Al-corrole forms a complex with methyl-viologen. Upon formation of this complex, fluorescence is quenched almost completely.

Analysis of the transient absorption spectra shows viologen-radical absorption and rapid loss of excited state population. This indicates ultrafast electron transfer dynamics.

For comparison we also investigated the dynamics of the corrole without methyl viologen, which exhibits fluorescence signals with a risetime of 10 ps. Our data provide information on various significant energy relaxation pathways in these type of molecules.

MO 23.5 Fri 15:00 BEBEL HS213

Femtosecond ionization dynamics of N₂ studied by wavelength-selected XUV pulses

— ●MARTIN ECKSTEIN¹, CHUNG-HSIN YANG¹, HANS-HERMANN RITZE¹, FABIO FRASSETTO², LUCA POLETTO², MARC VRAKING¹, and OLEG KORNILOV¹ — ¹Max-Born-Institut, Berlin, Germany — ²CNR-IFN, Padova, Italy

Studies of dissociative ionization of N₂ have a long history both for the purpose of atmospheric research and as tests of novel experimental methods and theoretical approaches to the problem of electron correlations. A prominent example is the inner valence photoionization of N₂ in the extreme ultraviolet (XUV) region of photon energies. The molecular electronic states in this region (30-50 eV) are strongly correlated and dissociate on femtosecond time scales. Despite the long history of research, the pose significant challenges for ab initio theories deterring complete explanation of the ionization dynamics. We present a novel approach using a time-compensating XUV monochromator in combination with an HHG source. The monochromator allows us to generate wavelength-selected femtosecond XUV pulses to initiate the dynamics, which is probed by multiphoton ionization by 800 nm. The time resolved photoelectron and photoion spectra recorded for six XUV photon energies between 32 eV and 50 eV reveal changes in branching ratios of several ionization channels, both resonant and non-resonant to the photon energy. The transient signals help us to identify major dissociative channels and follow the dynamics in real time. Preliminary ab initio calculations with extended basis sets will be presented and compared with experimental results.

MO 23.6 Fri 15:15 BEBEL HS213

Selective excitation of electronic states in K₂

— ●HENDRIKE BRAUN¹, DOMINIK PENDEL², CRISTIAN SARPE¹, 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

Recently we reported on the selective excitation of K₂ using spectrally phase-shaped femtosecond laser pulses [1]. Here we present data about the controlled excitation of the same molecule by optimized double pulse sequences [2]. In addition first experimental evidence shows that femtosecond laser pulses that are shaped with spectral phases consisting of second and third order polynomial modulation [3] offer a high degree of control over the populations in selected electronic states of the potassium dimer. A detailed analysis of quantum dynamic simulations reveals different mechanisms at play.

- [1] T. Bayer *et al.*, Phys. Rev. Lett. **110**, 123003 (2013)
 [2] M. Wöllenhaupt *et al.*, JPPA **180**, 248 (2006)
 [3] J. Schneider *et al.*, Phys. Chem. Chem. Phys. **13**, 8733 (2011)

MO 23.7 Fri 15:30 BEBEL HS213

Imaging valence electron motion during pericyclic reactions via time-resolved X-ray scattering — •TIMM BREDMANN, MIKHAIL IVANOV, and GOPAL DIXIT — Max-Born-Institut, Max-Born-Straße 2A, 12489 Berlin, Germany

Shooting the ultrashort, high-resolution movie of molecular processes is a long-standing dream of physicists, chemists and biologists, the realization of which will extend the understanding and hence the con-

trolability of chemical reactions in synthesis and bioscience. Here, we show by means of quantum mechanical ab-initio simulations how time-resolved X-ray scattering can be used to achieve this goal. We introduce a new technique for reconstructing the electron density from the time-resolved scattering pattern using only information of weakly scattered photons, thereby filtering out major contributions of core and inert valence electrons, yielding direct insight into the making and breaking of chemical bonds in complex molecules. Taking the Cope rearrangement of semibullvalene as explicit example, we demonstrate that this technique provides direct experimental access to the long-standing problem of synchronous vs. asynchronous bond making and bond breaking in pericyclic reactions, which has solely been investigated theoretically up to date.

MO 24: Biomolecules 2

Time: Friday 14:00–15:30

Location: BEBEL SR144

MO 24.1 Fri 14:00 BEBEL SR144

IRMPD spectra of metal-lumichrome ionic complexes — •PABLO NIETO¹, ALAN GÜNTHER¹, SOPHIE SEIDENBECHER¹, JUDITH LANGER¹, GIEL BERDEN², JOS OOMENS², and OTTO DOPFER¹ — ¹Institut für Optik und Atomare Physik Technische Universität Berlin, Hardenbergstr. 36, D-10623 Berlin, Germany — ²Radboud University Nijmegen Institute for Molecules and Materials, FELIX facility, Toernooiveld 7, 6525 ED Nijmegen, The Netherlands

Flavins are a fundamental class of biomolecules with a lumichrome (LC) chromophore. This family of molecules is involved in many important biological processes. To understand these phenomena at the molecular level, spectroscopic studies of isolated flavins and their complexes are required. We report IRMPD spectra of mass selected $\text{Me}^{q+}\text{-LC}$ ($\text{Me}^{q+} = \text{Li}^+, \text{Na}^+, \text{K}^+, \text{Rb}^+, \text{Cs}^+, \text{Mg}^{2+}$ and Ag^+) ionic complexes in the fingerprint range ($800\text{-}1900\text{ cm}^{-1}$) recorded in a FT-ICR-MS ion trap coupled to the free electron laser FELIX. In the liquid phase, flavins preferentially bind to positions at N5 and O4 [2]. In contrast, the additional O2 binding site was identified in our experiments. Furthermore, the spectra for Li^+ and Ag^+ are very similar, suggesting that both ions have comparable binding energies to LC. Finally, Mg^{2+} ions form strongly-bound $\text{Mg}^{2+}\text{-(LC)}_2$ complexes in a T-shaped structure. The large IRMPD linewidth ($>15\text{ cm}^{-1}$) due to the ion temperature (300 K) poses a limitation to these experiments. This limitation will be overcome with our new apparatus equipped with an ESI source and a cryogenic 22-pole ion trap (4 K) where single photon absorption spectroscopy will be carried out.

MO 24.2 Fri 14:15 BEBEL SR144

The α -Helix Motif in β -Peptides — FRANZISKA SCHUBERT¹, KEVIN PAGEL¹, MARIANA ROSSI^{1,2}, STEPHAN WARNKE¹, GERT VON HELDEN¹, VOLKER BLUM^{1,3}, •CARSTEN BALDAUF¹, and MATTHIAS SCHEFFLER¹ — ¹Fritz-Haber-Institut der MPG, Berlin, Germany — ²Physical and Theoretical Chemistry, University of Oxford, U.K. — ³MEMS, Duke University, Durham, U.S.A.

The natural α -helix motif is important in protein-protein recognition and binding. Its imitation by non-natural peptides may open route to modulators of protein interactions. In order to identify the prominent α -helix-motif also in β -peptides, we compare the conformational preferences of peptides $\text{Ac-(Xaa)}_6\text{-LysH}^+$, with Xaa being the α -amino acid alanine (peptide $\text{P}\alpha$) or its β -equivalent homo-alanine (peptide $\text{P}\beta$) that contains one more methylene unit than the α -building block. Such polyalanine-peptides were developed by Jarrold and co-workers to form α -helices in the gas phase.[1] Conformational space of $\text{P}\alpha$ and $\text{P}\beta$ was sampled globally by force field replica-exchange molecular dynamics (REMD) and then refined locally by *ab initio* REMD with the PBE functional corrected for long-range dispersion. $\text{P}\alpha$ is found to be mostly α -helical in the gas-phase at 300K.[2] Considering harmonic free energy corrections for $\text{P}\beta$, we find helical and non-helical conformers in the low free-energy regime. Helices are strongly stabilized by vibrational free energy. The combination of simulations with vibrational spectra and collision cross sections provides the first evidence for the α -helix motif in β -peptides. [1] Hudgins, Ratner, Jarrold: JACS 120, 12974 (1999); [2] Rossi, Scheffler, Blum: JPCB 117, 5574 (2013).

MO 24.3 Fri 14:30 BEBEL SR144

Two color enhanced IRMPD spectroscopy of mononuclear $\text{Ag(I)}/\text{Cu(I)}$ -Bispyridine-complexes — •JOACHIM HEWER,

MAXIMILIAN GAFFGA, YEVGENIY NOSENKO, and GEREON NIEDNER-SCHATTEBURG — 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 set of mononuclear transition metal complexes $[\text{HP-M-AP}]^+$ ($\text{HP} = 2\text{-Hydroxypyridine}, 3\text{-Hydroxypyridine}; \text{AP} = 2\text{-Aminopicoline}; \text{M} = \text{Ag}, \text{Cu}$), which serve as model systems for intramolecular energy transfer across the metal center. 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. The specific fragmentation behavior provides some insight into vibrational mode couplings beyond ergodicity.

[1] Y. Nosenko, F. Menges and C. Riehn, G. Niedner-Schatteburg, PCCP, 2013, 8171-8178.

[2] M. Gaffga, J.I. Lang, F. Menges, K. Muller, W. Thiel, G. Niedner-Schatteburg, 2013, manuscript in preparation.

MO 24.4 Fri 14:45 BEBEL SR144

Infrared Photodissociation Spectroscopy of Microsolvated β -phenethylamine Cation Complexes in the Gas Phase — •MARKUS SCHÜTZ, AUDE BOUCHET, ALEXANDER KLEMT, and OTTO DOPFER — Institut für Optik und Atomare Physik, TU Berlin, Hardenbergstr. 36, 10623 Berlin, Germany

Neurotransmitters have important biological functions and play an important role in human behaviour. The molecule β -phenethylamine (PEA) is the simplest aromatic biogenic ethylamino neurotransmitter. It acts as a backbone of numerous hallucinogen substances and as a model for more complex neurotransmitters. Infrared photodissociation (IRPD) spectra of the Ar- and H_2O -tagged PEA cation complexes are recorded to study the conformation and microsolvation in nonpolar and polar environment. Comparison with simulated vibrational spectra from density functional theory allows for the assignment of different isomers and reveals some surprising insights into geometrical structures.

MO 24.5 Fri 15:00 BEBEL SR144

Gas-Phase Spectroscopy of Conformer-Selected Proteins — •STEPHAN WARNKE, KEVIN PAGEL, and GERT VON HELDEN — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

Mass spectrometry (MS) is a key technique to investigate biomolecules in the gas phase and many methods are available to obtain mass/charge ratios with very high accuracy. In combination with gas-phase spectroscopy, information about the molecules' composition and local structure can be obtained. However, the overall 3-dimensional structure of the molecule cannot be investigated with these methods alone - even though their knowledge is crucial for the understanding of intra- and inter- molecular interactions as well as the function of the molecule in the living organism. Additionally, peptides and proteins can coexist in a multitude of different conformations in the gas phase and it is not clear in how far this structural heterogeneity does affect the

above mentioned methods. A technique that is sensitive to the higher order structure of gas-phase ions is ion mobility spectrometry (IMS). In IMS the absolute (angle averaged) collision cross section and, thus, the effective size of the ion is determined. When molecules coexist in different conformations, they can be separated in space and time to allow for experiments on both mass/charge as well as shape/charge selected biomolecular ions.

In this talk, first results of spectroscopic experiments on mass/charge and conformer selected gas-phase proteins will be presented.

MO 24.6 Fri 15:15 BEBEL SR144

Binding motifs of a microsolvated neurotransmitter: IR spectroscopy of Ar-tagged protonated phenylethylamine and its water clusters — •AUDE BOUCHET, MARKUS SCHÜTZ, and OTTO DOPFER — Institut für Optik und Atomare Physik, Technische Universität Berlin, Germany

The characterization of the three-dimensional structure of biologically relevant molecules, the role played by inter- and intramolecular inter-

actions, especially with water which is the ubiquitous solvent in biological media, and their ability to form charged groups, are key issues to be addressed to deepen the understanding of recognition phenomena at the molecular level in biological environments. Biomolecules are generally not neutral in physiological medium, but protonated or zwitterionic. The conformation of these charged molecules and their solvation shell is thereby modified compared to neutral species. Here, vibrational spectroscopy, associated with quantum chemical calculations, has been applied on a protonated neurotransmitter, phenylethylamine (H^+PEA), and its water clusters isolated in the gas phase. The results obtained on the Ar-tagged H^+PEA show that a strong intramolecular $NH \cdots \pi$ interaction induces conformational locking of the monomer into a folded structure. Monohydrated H^+PEA reveals that a very stable inclusion structure is experimentally generated, in which the water molecule is inserted between the positively charged amino group and the phenyl moiety of H^+PEA . This ligand acts both as an hydrogen bond acceptor ($NH \cdots O$) and hydrogen bond donor ($OH \cdots \pi$). A second isomer, for which the water is H bonded to a "surface" NH group is also found.