

Molecular Physics Division Fachverband Molekülphysik (MO)

Stefan Lochbrunner
Institut für Physik, Universität Rostock
Albert-Einstein-Str. 23
18059 Rostock
stefan.lochbrunner@uni-rostock.de

Overview of Invited Talks and Sessions

(Lecture rooms N 6 and N 25; Poster P OGs)

Invited Talks

MO 1.1	Mon	14:30–15:00	N 6	Dynamic Solvent Effects Treated with a Quantum/Classical TDSCF Approach — •MARTIN PESCHEL, JULIUS ZAULECK, FLORIAN ROTT, REGINA DE VIVIE-RIEDLE
MO 3.1	Mon	17:00–17:30	N 6	Single-shot coherent diffractive imaging of individual clusters using a high harmonic source — NILS MONSERUD, DANIELA RUPP, BRUNO LANGBEHN, MARIO SAUPPE, JULIAN ZIMMERMANN, YEVHENIY OVCHARENKO, THOMAS MÖLLER, FABIO FRASSETTO, LUCA POLETTI, ANDREA TRABATTONI, FRANCESCA CALGARI, MAURO MISOLI, KATHARINA SANDER, CHRISTIAN PELTZ, MARC J.J. VRAKING, THOMAS FENNEL, •ARNAUD ROUZÉE
MO 5.1	Tue	11:00–11:30	N 6	Cryo Kinetics and Spectroscopy of 3d Metal Clusters and Alloys — JENNIFER MOHRBACH, SEBASTIAN DILLINGER, MATTHIAS KLEIN, AMELIE EHRHARD, •GEREON NIEDNER-SCHATTEBURG
MO 6.1	Tue	11:00–11:30	N 25	Illuminating Molecular Symmetries with Bicircular High-Order-Harmonic Generation — •DANIEL M. REICH, LARS BOJER MADSEN
MO 7.1	Tue	14:30–15:00	N 6	Cluster Studies with the BerlinTrap — •PABLO NIETO, ALAN GÜNTHER, DAVID MÜLLER, ALEX SHELDRIK, OTTO DOPFER
MO 8.1	Tue	14:30–15:00	N 25	Ultrafast dynamics of a magnetically bistable molecular switch by fs transient absorption spectroscopy — •SEBASTIAN MEGOW, JULIA BAHRENBURG, HENDRIK BÖHNKE, MATS BOHNSACK, MARK DITTNER, MARCEL DOMMASCHK, RAINER HERGES, FRIEDRICH TEMPS
MO 10.1	Wed	14:30–15:00	N 6	Molecular movies of migrating protons on different paths — •HEIDE IBRAHIM, VINCENT WANIE, SAMUEL BEAULIEU, BENJI WALES, BRUNO SCHMIDT, XIAO-MIN TONG, JOE SANDERSON, MICHAEL SCHURMAN, FRANÇOIS LÉGARÉ
MO 13.1	Thu	11:00–11:30	N 6	Ultrafast solvent fluctuations steer the hydrated excess proton in the Zundel cation H_5O_2^+ — •FABIAN DAHMS, RENE COSTARD, EHUD PINES, EVA MARIA BRÜNING, TORSTEN SIEBERT, BENJAMIN P. FINGERHUT, ERIK T. J. NIBBERING, THOMAS ELSAESSER
MO 15.1	Thu	14:30–15:00	N 6	Tracking electronic processes inside dense matter by luminescence — •ANDRÉ KNIE
MO 17.1	Fri	11:00–11:30	N 6	Molecular-Frame Photoelectron Imaging of Controlled Complex Molecules — •JOSS WIESE, SEBASTIAN TRIPPEL, JOCHEN KÜPPER

Invited talks of the joint symposium SYDD

See SYDD for the full program of the symposium.

SYDD 1.1	Mon	14:30–15:00	P 1	Controlling (?) Quantum Dynamics with Open Systems — •DIETER MESCHÉDE
SYDD 1.2	Mon	15:00–15:30	P 1	Many-body physics of driven, open quantum systems: optically driven Rydberg gases — •MICHAEL FLEISCHHAUER
SYDD 1.3	Mon	15:30–16:00	P 1	Theorie getriebener dissipativer Quantensysteme / theory of driven dissipative quantum systems — •TOBIAS BRANDES

SYDD 1.4	Mon	16:00–16:30	P 1	Calorimetry of a Bose-Einstein-condensed photon gas — •MARTIN WEITZ
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Invited talks of the joint symposium SYAD

See SYAD for the full program of the symposium.

SYAD 1.1	Wed	11:00–11:30	RW 1	Exciton transport in disordered organic systems — •FRANZISKA FENNEL
SYAD 1.2	Wed	11:30–12:00	RW 1	Quantum dynamics in strongly correlated one-dimensional Bose gases — •FLORIAN MEINERT
SYAD 1.3	Wed	12:00–12:30	RW 1	Dynamics and correlations of a Bose-Einstein condensate of light — •JULIAN SCHMITT
SYAD 1.4	Wed	12:30–13:00	RW 1	Circular dichroism and accumulative polarimetry of chiral femtochemistry — •ANDREAS STEINBACHER

Invited talks of the joint symposium SYAM

See SYAM for the full program of the symposium.

SYAM 1.1	Thu	11:00–11:30	P 1	Buffer gas cooling of antiprotonic helium to T=1.5-1.7 K, and the antiproton to electron mass ratio — •MASAKI HORI
SYAM 1.2	Thu	11:30–12:00	P 1	The BASE Experiment: High-precision comparisons of the fundamental properties of protons and antiprotons — •C. SMORRA, M. BESIRLI, K. BLAUM, M. BOHMAN, M. J. BORCHERT, J. HARRINGTON, T. HIGUCHI, H. NAGAHAMA, Y. MATSUDA, A. MOOSER, C. OSPELKAUS, W. QUINT, S. SELLNER, G. SCHNEIDER, N. SCHOEN, T. TANAKA, J. WALZ, Y. YAMAZAKI, S. ULMER
SYAM 1.3	Thu	12:00–12:30	P 1	Antihydrogen physics at the ALPHA experiment — •NIELS MADSEN
SYAM 2.1	Thu	14:30–15:00	P 1	Muon g-2 — •KLAUS JUNGSMANN
SYAM 2.2	Thu	15:00–15:30	P 1	Antihydrogen physics at ASACUSA and AEGIS — •CHLOÉ MALBRUNOT
SYAM 2.3	Thu	15:30–16:00	P 1	An experiment to measure the anti-hydrogen Lamb shift — •PAOLO CRIVELLI

Sessions

MO 1.1–1.7	Mon	14:30–16:30	N 6	Photochemistry
MO 2.1–2.8	Mon	14:30–16:30	N 25	Precision Experiments on Small Molecules
MO 3.1–3.6	Mon	17:00–18:45	N 6	Diffraction and Coherences (with A)
MO 4.1–4.8	Mon	17:00–19:00	N 25	Spectroscopy of Cold Molecules and Complexes
MO 5.1–5.7	Tue	11:00–13:00	N 6	Clusters I (with A)
MO 6.1–6.6	Tue	11:00–12:45	N 25	Theory of Molecular Dynamics
MO 7.1–7.6	Tue	14:30–16:15	N 6	Helium Droplets and Systems (with A)
MO 8.1–8.7	Tue	14:30–16:30	N 25	Fast Intramolecular Dynamics
MO 9.1–9.20	Tue	17:00–19:00	P OGs	Posters 1: Dichroism, VUV and Xray, Clusters, and Cold Molecules
MO 10.1–10.7	Wed	14:30–16:30	N 6	Highly Excited Molecules and Clusters
MO 11.1–11.8	Wed	14:30–16:30	N 25	Molecular Nanostructures and Solids
MO 12.1–12.20	Wed	17:00–19:00	P OGs	Posters 2: Molecular Dynamics, Clusters, and High Resolution Spectroscopy
MO 13.1–13.7	Thu	11:00–13:00	N 6	Probing Vibrations
MO 14.1–14.8	Thu	11:00–13:00	N 25	Theory of Coupled Systems
MO 15.1–15.7	Thu	14:30–16:30	N 6	Environment Controlled Processes
MO 16.1–16.20	Thu	17:00–19:00	P OGs	Posters 3: Experimental Techniques and Theoretical Approaches
MO 17.1–17.7	Fri	11:00–13:00	N 6	Experimental Techniques
MO 18.1–18.8	Fri	11:00–13:00	N 25	Biomolecules and Electron Transfer
MO 19.1–19.7	Fri	11:00–13:00	N 3	Clusters II (with A)
MO 20.1–20.7	Fri	14:30–16:30	N 3	Clusters III (with A)

Annual General Meeting of the Molecular Physics Division

Tuesday 13:15–14:00 N 6

MO 1: Photochemistry

Time: Monday 14:30–16:30

Location: N 6

Invited Talk

MO 1.1 Mon 14:30 N 6

Dynamic Solvent Effects Treated with a Quantum/Classical TDSCF Approach — ●MARTIN PESCHEL, JULIUS ZAULECK, FLORIAN ROTT, and REGINA DE VIVIE-RIEDLE — Ludwig-Maximilians-University, Munich, Germany

The simulation of quantum dynamics on potential energy surfaces is a powerful tool to examine chemical reactions. The course of these reactions might be substantially altered in solution. A coupled quantum dynamics/molecular dynamics approach (cQD/MD) is presented to introduce solvent effects into the simulations. It treats the solvent by classical molecular dynamics and couples this classical system to the quantum solvated molecule in a time-dependent self-consistent fashion. We discuss the solvent-induced changes in wavepacket coherence and dispersion of the quantum system. As an example, the photodissociation of ICN in liquid argon is considered in detail with an outlook on more complex systems.

MO 1.2 Mon 15:00 N 6

Photocleavage of coumarin dimers studied by uv ultrafast transient absorption spectroscopy — ●MAN JIANG¹, NICHOLAS PAUL¹, NIKOLAI BIENIEK², TIAGO BUCKUP¹, NORBERT HAMPP², and MARCUS MOTZKUS¹ — ¹Institute of Physical Chemistry, Im Neuenheimer Feld 229, University of Heidelberg, D-69120 Heidelberg — ²Department of Chemistry, Hans-Meerwein-Str. 4, University of Marburg, D-35032 Marburg

The photoinduced cleavage of a coumarin dimer into its two monomers is a promising mechanism for laser controlled medical applications. In order to understand the underlying dynamics of the cleavage reaction in details and develop strategies for an increase of the reaction efficiency, UV transient absorption spectroscopy was applied to three unsubstituted coumarin dimer isomers, the anti-head-to-head dimer, the syn-head-to-head dimer and the syn-head-to-tail dimer. The experiments performed under 280 nm pumping and broadband (300–650 nm) probing reveal that the cleavage reaction of coumarin dimers occurs via non-radiative short-lived singlet states. Two branched kinetic models were developed, which describe the formation of monomers and relaxation dynamics of dimers, from which we were able to explore the precise time-scale of coumarin monomers formation and the quantum yields of the dimer splitting. The anti-hh dimer shows the highest cleavage efficiency with a value of about 20 %. The differences of cleavage efficiency for three dimer isomers are interpreted in terms of different steric hindrances of substitution groups attached to the cyclobutane ring and charge delocalization on the intermediate state.

MO 1.3 Mon 15:15 N 6

Spectroscopic Investigation of a Cr-Complex on the fs-Time Scale — ●ALEKSEJ FRIEDRICH¹, SVEN OTTO², CHRISTOPH FÖRSTER², CHRISTOPH KREITNER², KATJA HEINZE², and STEFAN LOCHBRUNNER¹ — ¹Institute of Physics, University of Rostock, Germany — ²Institute of Inorganic and Analytical Chemistry, Johannes Gutenberg-University of Mainz, Germany

Ultrafast spectroscopy is performed on the metal complex [Cr(ddpd)₂][BF₄]₃ (ddpd: N,N'-dimethyl-N,N'-dipyridine-2-ylpyridine-2,6-diamine). The compound is an interesting candidate for NIR OLEDs, fiber-optic telecommunication applications, night-vision readable displays, oxygen sensing, and in vivo imaging. The molecule is water soluble and exhibits strong and extremely long living photo luminescence around 775 nm [1]. While the ground state is a quartet state the emitting state is a doublet. The intermolecular processes after excitation are not fully understood. We carried out fs-transient-absorption and streak-camera measurements to investigate these processes. We found a fast population of the lowest emitting doublet state within 6 ps and a luminescence lifetime of 840 μs. No indication for stimulated emission was observed. This indicates that the intersystem crossing between the quartet and doublet manifold occurs within our time resolution of 100 fs and the 6 ps dynamics is due to relaxation within the doublet manifold.

[1] S. Otto et al., *Angew. Chem. Int. Ed.*, 54, 11572 (2015).

MO 1.4 Mon 15:30 N 6

The Photodissociation of the ortho- & para-Xylyl Radical, C₈H₉, Investigated by Velocity Map Imaging — ●KAI PACH-

NER and INGO FISCHER — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Deutschland

Xylyl radicals can be found as intermediates in combustion processes. Their parent molecules, the xylenes, are used as additives in fuels to increase antiknock properties. The thermal decomposition of the xylyl radicals has been explored recently by Hemberger et al. in a synchrotron experiment [1]. Based on these studies, we investigated the photodissociation of the ortho- & para-xylyl radical using velocity map imaging. Xylyl radicals were formed via flash pyrolysis in a pulsed molecular beam using 2-/4-methylphenethyl nitrite as a precursor. Irradiation of the xylyl radical with UV light around 310 nm leads to the formation of the corresponding xylenes for both radicals, or benzocyclobutene for the ortho-xylyl radical respectively, by hydrogen atom loss. Generated hydrogen fragments are then ionized in a [1+1']-REMPI process via the 1s-2p transition and detected on a velocity map imaging detector. The translational energy distribution of the hydrogen fragments as well as their angular distribution and rate constants for the hydrogen atom loss indicate a statistical dissociation in the ground state or an indirect dissociation in the excited state.

[1] Hemberger et al., *J. Phys. Chem. A*, 2014, 118, 3593 - 3604.

MO 1.5 Mon 15:45 N 6

Dynamical studies on the photodissociation of diphenylmethyl bromide — ●FRANZISKA SCHÜPPEL, MATTHIAS K. ROOS, and REGINA DE VIVIE-RIEDLE — Department Chemie, Ludwig-Maximilians-Universität München

Carboradicals and -cations are key intermediates for many chemical reactions. They may be generated by UV-laser excitation of carbohalide compounds such as diphenylmethyl bromide. Here, a local $\pi - \pi^*$ excitation occurs, followed by the C-Br bond cleavage leading to radical or ion pairs within a femtosecond timescale.

We use both, quantum dynamical and semiclassical on-the-fly dynamical methods to simulate the reaction. In both approaches we employ an ONIOM two-layer method with CASSCF as high level method. In the quantum dynamics we take the solvent environment into account using the Dynamic Continuum ansatz [1] developed in our group.

We verify for both simulations the decisive role of two consecutive conical intersections for the product splitting, like we recently showed [2] for chlorine as leaving group. Nonetheless, we report remarkable differences compared to the chlorine case and we especially discuss the role of the pyramidalization of the central carbon atom. We evaluate product ratio and delay times for both approaches and compare them with experimental results.

[1] S. Thallmair et al., *J. Phys. Chem. Lett.* **5** (2014), 3480–3485.

[2] S. Thallmair et al., *Struct. Dyn.* **3** (2016), 043205.

MO 1.6 Mon 16:00 N 6

Time-Resolved Step-Scan FTIR Investigations on Dinuclear Cu(I)-NHETPHOS-complexes — ●MANUEL ZIMMER¹, FABIAN DIETRICH¹, FLORIAN BÄPPLER¹, MANUELA WALLECH², DANIEL VOLZ³, STEFAN BRÄSE², ROLF DILLER¹, and MARKUS GERHARDS¹ — ¹TU Kaiserslautern, 67663 Kaiserslautern — ²Karlsruhe Institute of Technology, 76131 Karlsruhe — ³CYNORA GmbH, 76646 Bruchsal

Time-resolved (TR) infrared experiments enable the investigation of chemical reactions, photochemical/-physical processes and their kinetic traces. With the step-scan technique we are able to identify electronically excited states and excited state structures by comparison with theoretical results from quantum chemical calculations. Here we present the first TR step-scan FTIR measurements on dimetallic Cu(I)-NHETPHOS-complexes in solid state (KBr matrix and thin film). These complexes, which are developed for emitter material in OLEDs, are a very promising substitute for currently used Ir-complexes. Time-resolved IR spectra of electronically excited states have been obtained by step-scan FTIR measurements and in addition, wavelength and temperature dependent measurements as well as femtosecond transient absorption and reflectivity measurements have been performed to gain detailed information about the excited state processes and deactivation mechanisms. The temperature dependent measurements down to 20 K provided valuable information to confirm the postulated thermally activated delayed fluorescence (TADF) mechanism at room temperature (RT). The interpretation of measured spectra succeeded in combina-

tion with quantum chemical calculations (DFT and TD-DFT).

MO 1.7 Mon 16:15 N 6

New Insights into the Photodissociation of Bisphenyl(2,4,6-trimethylbenzoyl)phosphine oxide — ●STEFFEN STRAUB, CARA TABEA LOHRMANN, JÖRG LINDNER, and PETER VÖHRINGER — Rheinische Friedrich-Wilhelms-Universität Bonn

Benzoylphosphine oxides are widely known as industrial photoinitiators in photochemical curing processes. In the recent past, their photochemistry and photophysics have been studied, for example by Picosecond Pump Probe Spectroscopy. These efforts suggested a C-P-bond breakage taking place on a time scale of hundred picoseconds and being facilitated by an S_1 - T_1 intersystem crossing.

Here, we unravel the primary processes of the photoinitiator

Bisphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (BTPO) in great detail, using femtosecond UV-pump IR-probe spectroscopy. All experiments were carried out using pump pulses of 100 fs duration, centered at a wavelength of $\lambda = 380$ nm.

We found that the formation of the benzoyl radical occurs in a delayed fashion and cannot be fit to first order growth kinetics, as was assumed previously. A careful analysis of the spectro-temporal evolution in the mid-infrared region yields accurate time constants of 20 ps and 120 ps for the initial S_1 - T_1 intersystem crossing and the ensuing α -cleavage with radical pair formation, respectively. Moreover, we were able to identify the C=C-stretching mode of the benzoyl radical in liquid solution, which has been accomplished previously only in the gaseous phase or through complex cryogenic matrix isolation techniques.

MO 2: Precision Experiments on Small Molecules

Time: Monday 14:30–16:30

Location: N 25

MO 2.1 Mon 14:30 N 25

Doppler-limited precision spectroscopy of cold formaldehyde in an electric trap — ●MARTIN IBRÜGGER, ALEXANDER PREHN, MARTIN ZEPPENFELD, and GERHARD REMPE — Max-Planck-Institut für Quantenoptik, Hans-Kopfermann-Str. 1, 85748 Garching

Besides cooling, trapping has proven to be a key ingredient for high precision spectroscopy of many atomic species as can be seen in e.g. various optical clock experiments around the world. For molecules however, in particular polyatomic molecules, there are few to none experiments in a trap employing cooling to cold temperatures to increase control and reduce linewidths.

Here, we present microwave spectroscopy on a magic transition between rotational levels of trapped formaldehyde. The molecules are stored in an electric trap [1] and cooled via optoelectrical Sisyphus cooling [2] to temperatures ranging from 60 mK to 2 mK. We achieve Doppler-limited linewidths down to 3.8 kHz corresponding to an accuracy of 10^{-8} . The lineshapes are in excellent agreement with theory taking into account the energy distribution of the molecules and the electric field distribution of the trap. These results show the feasibility of high precision spectroscopy in our experiment and open up the way to measurements with unprecedented precision for polyatomic molecules once applied to even colder ensembles.

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

[2] A. Prehn *et al.*, *Phys. Rev. Lett.* **116**, 063005 (2016).

MO 2.2 Mon 14:45 N 25

Photodetachment study of NH_2^- ions in the 22 pole trap — ●OLGA LAKHMANSKAYA¹, MALCOLM SIMPSON¹, SIMON MURAUER¹, VIATCHESLAV KOKOULINE², and ROLAND WESTER¹ — ¹Universität Innsbruck, Innsbruck, Austria — ²University of Central Florida, Orlando, US

We present a near-threshold photodetachment spectrum of the amide anion NH_2^- performed in a cold (10 K) 22-pole ion trap. The spectrum shows steps in the relative cross section that are associated with the transitions between rotational levels of the vibrational ground states of NH_2^- (X^1A_1 electronic state) and NH_2 (X^2B_1 electronic state). With this data we can significantly improve the determination of the electron affinity of amidogen NH_2 .

MO 2.3 Mon 15:00 N 25

Crossed-beam velocity-map-imaging of the $Ar^+ + H_2$ charge-transfer reaction — ●TIM MICHAELSEN¹, BJÖRN BASTIAN¹, JENNIFER MEYER¹, EDUARDO CARRASCOA², DAVE PARKER³, and ROLAND WESTER¹ — ¹Universität Innsbruck, Austria — ²University of Melbourne, Australia — ³Radboud University, Nijmegen, Netherlands

The Reaction of $Ar^+ + H_2$ can proceed via atomic re-arrangement resulting in $ArH^+ + H$ or via charge transfer resulting in $Ar + H_2^+$. Here we will focus on the charge transfer pathway. Previous studies on this pathway predict a strong dependence of the reaction rate on the spin-orbit state of the Ar^+ [1] and previous crossed-beam studies predict forward scattering with a large backward scattered fraction at low collision energies [2]. Additionally, theory and experiments predict a quasi-resonant behavior towards the product ion vibrational state $H_2^+(v=2)$ [3].

Here, we present differential cross-sections obtained with a crossed-beam VMI-spectrometer for charge transfer reactions of Ar^+ with H_2 at energies below 1 eV. We observe predominantly forward scattering, a dependence on the Ar^+ spin-orbit state as well as dominant excitation of the $H_2^+(v=2)$ state. Additionally, we compare these results to the charge-transfer reaction with D_2 , N_2 [4] and O_2 .

[1] Tanaka K., *et al.* *J. Chem. Phys.* **75**.10 (1981): 4941-4945. [2] Hierl P., *et al.* *J. Chem. Phys.* **67**.6 (1977): 2678-2686. [3] Baer M., *et al.* *J. Chem. Phys.* **93**.7 (1990): 4845-4857. [4] Trippel S., *et al.* *PRL* **110**.16 (2013): 163201.

MO 2.4 Mon 15:15 N 25

Experimental studies of the ion-molecule reactions $H_2^+ + H_2$ and $H_2^+ + D_2$ at low collision energies with a merged beam apparatus — ●KATHARINA HÖVELER, PITT ALLMENDINGER, JOHANNES DEIGLMAYR, OTTO SCHULLIAN, and FRÉDÉRIC MERKT — Laboratorium für Physikalische Chemie, ETH Zürich, CH-8093 Zurich, Switzerland

The exothermic, barrierless $H_2^+ + H_2 \rightarrow H_3^+ + H$ reaction has been studied in the collision-energy range $E_{\text{coll}}/k_B = 300 \text{ mK} - 50 \text{ K}$. To reach such low collision energies, we use a merged-beam approach and substitute the H_2^+ reactants by the ionic cores of H_2 molecules in high- n Rydberg-Stark states. The Rydberg electron does not influence the reaction but shields the ion from heating by space-charge effects and stray electric fields. Merging of the two pulsed reactant supersonic beams is achieved by photoexcitation of the molecules of one beam to high- n Rydberg-Stark states followed by Rydberg-Stark deceleration and deflection using a curved chip-based surface-electrode device. The collision energy is tuned by varying the temperature of the valve generating the H_2 ground-state beam for selected velocities of the H_2 Rydberg beam. The reaction cross section is found to follow the classical Langevin capture model down to $E_{\text{coll}}/k_B = 5 \text{ K}$. At lower temperatures, a deviation is observed and attributed to ion-quadrupole long-range interactions. Investigation of the reaction $H_2^+ + D_2$ enables us to distinguish between charge transfer, D atom transfer and H^+ ion transfer.

MO 2.5 Mon 15:30 N 25

Towards Reactive Scattering between Metastable Helium and Magneto-Optically Trapped Lithium — ●JONAS GRZESIAK, KATRIN DULITZ, ANDRIY ACHKASOV, FRANK STIENKEMEIER, and MARCEL MUDRICH — Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg i. Br.

The experimental study of Penning ionization reactions, i.e., the reactive scattering of metastable rare gas atoms with neutral species, has recently attracted a lot of attention through the observation of orbiting resonances at low collision energies [1]. We present first results leading to a detailed study of reactive scattering between supersonically expanded metastable helium atoms and ultracold lithium atoms confined in a magneto-optical trap. We also show that our cryogenically cooled source provides intense, velocity-tunable and cold supersonic beams of metastable helium atoms, and we discuss the efficiency of metastable atom production using two conceptually different, home-made discharge units.

[1] A. B. Henson, S. Gersten, Y. Shagam, J. Narevicius, E. Narevi-

cius, Science 338, 234 (2012).

MO 2.6 Mon 15:45 N 25

Nondestructive Detection of Polar Molecules via Rydberg Atoms — ●MARTIN ZEPPENFELD and FERDINAND JARISH — MPI für Quantenoptik, Hans Kopfermann Str. 1, 85748 Garching

Research on cold and ultracold molecules is impeded by the difficulty in many cases to efficiently detect molecules, with the choice of molecule species often influenced by the need for a suitable detection scheme. We demonstrate the possibility to efficiently and nondestructively detect basically any polar molecule species using Rydberg atoms [1]. A Rydberg atom senses the presence of a molecule based on Förster resonance energy transfer. We show that huge interaction cross sections of more than 10^{-6} cm² exist for low collision energies, allowing for efficient detection [1]. First results on detection of room temperature ammonia molecules with Rubidium Rydberg atoms will be presented.

[1] M. Zeppenfeld, arXiv:1611.08893 [physics.atom-ph] (2016).

MO 2.7 Mon 16:00 N 25

Laser cooling of molecular anions — ●SEBASTIAN GERBER¹, JULIAN FESEL¹, CHRISTIAN ZIMMER¹, INGMARI TIETJE¹, ALEXANDER HINTERBERGER¹, DANIEL COMPARAT², and MICHAEL DOSER¹ — ¹CERN, 127 Rute de Meyrin, Switzerland — ²Laboratoire Aime Cotton, CNRS, 91405 Orsay, France

Molecular anions play a central role in a wide range of fields: from atmospheric and interstellar science, anionic superhalogens to the chemistry of highly correlated systems. However, up to now the synthesis of negative ions in a controlled manner at ultracold temperatures relevant for the processes in which they are involved is currently limited to a few kelvin by supersonic beam expansion followed by resistive, buffer gas or electron cooling in cryogenic environments. We present a realistic scheme for laser cooling of C₂[−] molecules to subkelvin temperatures, which has been only achieved for a few neutral diatomics. The

generation of a pulsed source of C₂[−] and the subsequent laser cooling techniques of C₂[−] confined in a Penning trap are reviewed. Further, laser cooling one anions species would allow to sympathetically cool other molecular anions, electrons and antiprotons that are confined in the same trapping potential. In this presentation the status of the experiment and the feasibility of C₂[−] sympathetic Doppler laser cooling, photo-detachment cooling and AC Stark Sisyphus cooling will be reviewed.

MO 2.8 Mon 16:15 N 25

Trapping and Cooling of Polar Molecules: YO and OH — ●TIM LANGEN^{1,2}, DAVID REENS¹, HAO WU¹, ALEJANDRA COLLOPY¹, YEWELI WU¹, SHIQIAN DING¹, and JUN YE¹ — ¹JILA, NIST and University of Colorado, Boulder, USA — ²Physikalisches Institut und IQST, Universität Stuttgart, Germany

We present two experiments progressing towards directly trapping and cooling polar molecular gases to the millikelvin regime and below. First, using microwave mixing of rotational states and two vibrational repump lasers, we implement a cycling transition in the yttrium (II) monoxide (YO) molecule that is closed to the 10⁶ level [1]. With this cycling transition, a beam of YO from a two-stage cryogenic buffer gas cell is decelerated to less than 5 m/s, slow enough to be loaded into a three-dimensional magneto-optical trap. We plan to implement a second stage of narrow-line cooling to reach below 100 microkelvin [2]. Second, we present our progress in the magnetic trapping and cooling of a gas of the dipolar hydroxyl (OH) radical [3]. Using detailed studies of electric-field-induced losses, we identify a novel Majorana-like loss mechanism that is inherently connected to the dipolar nature of the molecules. We discuss a newly developed trap design that will mitigate this loss to enable further evaporative cooling.

[1] M. Yeo et al., Phys. Rev. Lett. **114**, 223003 (2015).

[2] A. L. Collopy et al., New J. Phys. **17**, 055008 (2015).

[3] B. K. Stuhl et al., Nature **492**, 396 (2012).

MO 3: Diffraction and Coherences (with A)

Time: Monday 17:00–18:45

Location: N 6

Invited Talk

MO 3.1 Mon 17:00 N 6

Single-shot coherent diffractive imaging of individual clusters using a high harmonic source — NILS MONSERUD¹, DANIELA RUPP², BRUNO LANGBEHN², MARIO SAUPPE², JULIAN ZIMMERMANN², YEVHENIY OVCHARENKO², THOMAS MÖLLER², FABIO FRASSETTO³, LUCA POLETTI³, ANDREA TRABATTONI⁴, FRANCESCA CALGARI⁵, MAURO MISOLI^{4,5}, KATHARINA SANDER⁶, CHRISTIAN PELTZ⁶, MARC J.J. VRAKING¹, THOMAS FENNEL⁶, and ●ARNAUD ROUZÉE¹ — ¹Max-Born-Institut, Berlin, Germany — ²Institut für Optik und Atomare Physik, Technische Universität Berlin, Berlin, Germany — ³CNR, Istituto di Fotonica e Nanotecnologie Padova, Padova, Italy — ⁴Department of Physics, Politecnico di Milano, Milano, Italy — ⁵CNR, Istituto di Fotonica e Nanotecnologie Milano, Milano, Italy — ⁶Institut für Physik, Universität Rostock, Rostock, Germany

We present a single-shot coherent diffractive imaging (CDI) experiment based on high harmonic generation of individual He nanodroplets performed with a table-top femtosecond extreme ultraviolet (XUV) light source. Using a laser based HHG source, we are able to demonstrate for the first time the possibility to extract the shape, size, and orientation of free-flying nanoparticles. While most of the recorded diffraction patterns are assigned to the formation of spherical nanodroplets, we observed as well non-point symmetric diffraction patterns which are uniquely assigned to the formation of prolate, pill-shaped He-nanodroplets. Our experiment paves the way towards time-resolved imaging of ultrafast electron motion in individual clusters and nanoparticles with attosecond time resolution.

MO 3.2 Mon 17:30 N 6

Numerical simulations for characterizing and optimizing an aerodynamic lens — ●NILS ROTH¹, SALAH AWEL^{1,2}, DANIEL HORKE^{1,3}, and JOCHEN KÜPPER^{1,2,3} — ¹Center for Free-Electron Laser Science, DESY, Notkestrasse 85, 22607 Hamburg, Germany — ²Department of Physics, University of Hamburg, Luruper Chaussee 149, 22761 Hamburg, Germany — ³The Hamburg Center for Ultrafast Imaging, Luruper Chaussee 149, 22761 Hamburg, Germany

Atomic resolution single-particle coherent diffractive imaging requires reproducible samples to reconstruct three-dimensional molecular structures from isolated particles [1]. Currently one of the major limiting factors is the inefficient delivery of particles and the correspondingly low number of strong diffraction patterns, collected during typical beam times. We build a numerical simulation infrastructure capable of calculating the flow of gas and the trajectories of particles through an entire aerosol injector, aiming to increase the fundamental understanding and to enable optimization of injection geometries and parameters. The simulation results are compared to literature studies and also validated against experimental data taken in an aerosol beam characterization setup [2]. The simulation yields a detailed understanding of the radial particle distribution and highlights weaknesses of current aerosol injectors. With the aid of these simulations we develop new experimental implementations to overcome current limitations and increase particle densities available for diffractive imaging experiments.

[1] M. M. Seibert, et al, Nature **470**, 78 (2011).

[2] Salah et al, Opt. Exp. **24**, 6507-6521 (2016)

MO 3.3 Mon 17:45 N 6

Femtosecond Diffractive Imaging of Coherent Nuclear Motion using Relativistic Electrons — JIE YANG¹, ●MARKUS GÜHR^{2,3}, XIAOZHE SHEN³, RENKAI LI³, THEODORE VECCHIONE³, RYAN COFFEE³, JEFF CORBETT³, ALAN FRY³, NICK HARTMANN³, CARSTEN HAST³, KAREEM HEGAZY³, KEITH JOBE³, IGOR MAKASYUK³, JOSEPH ROBINSON³, MATTHEW ROBINSON¹, SHARON VETTER³, STEPHEN WEATHERBY³, CHARLES YONEDA³, XIJIE WANG³, and MARTIN CENTURION¹ — ¹Department of Physics, University of Nebraska-Lincoln, Lincoln, NE, USA — ²Institut für Physik und Astronomie, Universität Potsdam, Potsdam, Germany — ³SLAC National Accelerator Laboratory, Menlo Park, CA, USA

Observing ultrafast changes in the molecular geometry after photoexcitation is crucial to understand the conversion of light energy into other energetic degrees of freedom within molecules. We present a time resolved electron diffraction study of a molecular vibrational wavepacket in photoexcited isolated iodine. We determine the time-varying inter-

atomic distance with a precision 0.07 Å and a temporal resolution of 230 fs full width at half maximum. The method is not only sensitive to the position but also the shape of the nuclear wave packet.

MO 3.4 Mon 18:00 N 6

Ultrashort polarization-tailored bichromatic fields — ●STEFANIE KERBSTADT, LARS ENGLERT, TIM BAYER, and MATTHIAS WOLLENHAUPT — Carl von Ossietzky Universität Oldenburg, Institut für Physik, Carl-von-Ossietzky-Straße 9-11, 26129 Oldenburg

Ultrashort bichromatic laser fields with commensurable center frequencies, have emerged as a powerful tool to coherently control the dynamics of free electron wave packets [1]. Here we present a novel scheme for the generation of polarization-tailored bichromatic laser fields based on ultrafast pulse shaping techniques. The scheme utilizes a 4f polarization pulse shaper equipped with a composite polarizer in the Fourier plane for independent amplitude and phase modulation of two spectral bands of a whitelight supercontinuum [2]. The setup allows us to sculpture the spectral amplitude, phase and polarization profile of both colors individually, offering an enormous versatility of producible bichromatic waveforms. In addition, the scheme features built-in dispersion management and the option for shaper-based pulse diagnostics. We demonstrate the fidelity of the generated bichromatic fields by optical characterization and present first results of quantum control of bichromatic photoionization of atoms employing photoelectron imaging tomography.

[1] D.B. Milosevic et al., Phys. Rev. A 61 (6) (2000), 063403.

[2] S. Kerbstadt et al., J. Mod. Opt., accepted (2016).

MO 3.5 Mon 18:15 N 6

Electronic decoherence following photoionization: full quantum-dynamical treatment of the influence of nuclear motion — ●CAROLINE ARNOLD^{1,2,3}, ORIOL VENDRELL^{1,3,4}, and ROBIN SANTRA^{1,2,3} — ¹Center for Free-Electron Laser Science, DESY, Notkestrasse 85, 22607 Hamburg, Germany — ²Department of Physics, University of Hamburg, Jungiusstrasse 9, 20355 Hamburg, Germany — ³The Hamburg Centre for Ultrafast Imaging, Luruper Chaussee 149, 22761 Hamburg, Germany — ⁴Department of Physics and Astronomy, Aarhus University, Ny Munkegade 120, 8000 Aarhus, Denmark

Photoionization using attosecond pulses can lead to the formation of

coherent superpositions of the electronic states of the parent ion. However, ultrafast electron ejection triggers not only electronic but also nuclear dynamics—leading to electronic decoherence, which is typically neglected on time scales up to tens of femtoseconds. We propose a full quantum-dynamical treatment of nuclear motion in an adiabatic framework, where nuclear wavepackets move on adiabatic potential energy surfaces expanded up to second order at the Franck-Condon point. We show that electronic decoherence is caused by the interplay of a large number of nuclear degrees of freedom and by the relative topology of the potential energy surfaces. Application to H₂O, paraxylene, and phenylalanine shows that an initially coherent state evolves to an electronically mixed state within just a few femtoseconds. In these examples, it is not the fast vibrations involving hydrogen atoms, but rather slow vibrational modes that destroy electronic coherence.

MO 3.6 Mon 18:30 N 6

Optimisation of strong laser field-free alignment using tailored light fields — ●EVANGELOS THOMAS KARAMATSKOS^{1,2}, SEBASTIAN RAABE⁴, ANDREA TRABATTONI¹, TERRY MULLINS¹, SEBASTIAN TRIPPEL^{1,2}, ARNAUD ROUZEE⁴, and JOCHEN KÜPPER^{1,2,3} — ¹DESY, Hamburg, Germany — ²Universität Hamburg, Germany — ³CUI, Hamburg, Germany — ⁴Max-Born Institute, Berlin, Germany

Alignment of molecules with respect to the laboratory fixed frame [1] enables the realization of a large variety of experiments such as the determination of molecular frame photoangular distribution (MFPAD's) [2] or laser induced electron diffraction (LIED) where typically a strong degree of alignment is needed [3]. We present a combined theoretical and experimental effort to optimise the degree of laser field-free alignment of molecules in the gas phase. We start by solving the time-dependent rotational Schrödinger equation coupled to a non-resonant laser field and a static electric field and use an iterative learning-loop algorithm to determine the ideal pulse shape that optimises the degree of alignment. These calculations serve as a guide to complement the experiments where the alignment laser pulse form is optimally tailored. We discuss the simulation results and the experimental realization of two-pulse impulsive alignment on the example of the linear molecule carbonyl sulfide (OCS) and give an outlook for the use of pulse shaping techniques to achieve strongly aligned asymmetric top molecules. [1] Stapelfeldt et al., Rev. Mod. Phys. 75, 543 (2003) [2] Hansen et al. Phys. Rev. Lett. 106, 073001 (2011) [3] Pullen et al., Nature Communications 6, 7262 (2015)

MO 4: Spectroscopy of Cold Molecules and Complexes

Time: Monday 17:00–19:00

Location: N 25

MO 4.1 Mon 17:00 N 25

C₆₀⁺ Near-IR Emissions: Astronomical Relevance. — ●DMITRY STRELNIKOV¹, BASTIAN KERN², and MANFRED KAPPES¹ — ¹Physikalische Chemie, KIT, Karlsruhe, Germany — ²MPI for Solid State Research, Stuttgart, Germany

Recently, five Diffuse Interstellar Bands (DIBs) were assigned to C₆₀⁺ [1,2]. While investigating C₆₀⁺ in various cryogenic matrixes, we have observed LIF in the near-IR, when exciting the near-IR vibronic bands of C₆₀⁺. Power dependence measurements revealed a one-photon LIF process. In contrast, excitation in the UV does not lead to the emission of C₆₀⁺ in the vicinity of its NIR absorptions. We propose to search for C₆₀⁺ near-IR emissions in the fullerene containing reflection nebulae.

References

1. Campbell, E. K., Holz, M., Gerlich, D., and Maier, J. P. 2015, Nature, 523, 322.

2. Walker, G. A. H., Bohlender, D. A., Maier, J. P., and E. K. Campbell. 2015, ApJL, 812, L8.

MO 4.2 Mon 17:15 N 25

Cryo IR spectroscopy of a tetranuclear cobalt carbonyl complex in isolation — ●SEBASTIAN DILLINGER¹, JENNIFER MOHRBACH¹, JOHANNES LANG¹, PIERRE BRAUNSTEIN², and GEREON NIEDNER-SCHATTEBURG¹ — ¹Fachbereich Chemie und Forschungszentrum OPTIMAS, Technische Universität Kaiserslautern, 67663 Kaiserslautern, Germany — ²Laboratoire de Chimie de Coordination, Institut de Chimie, UMR 7177 CNRS, Université de Strasbourg, 67081 Strasbourg, France

We present well resolved Infrared Multiple Photon Dissociation (IR-

MPD) spectra of isolated [Co₄(CO)_n(dppa-H⁺)]⁻ (n = 3 - 10, dppa = NH(PPh₂)₂) in the carbonyl stretching region at cryogenic temperatures (26 K). [1] The [Co₄(CO)₁₀(dppa-H⁺)]⁻ complex [2] serves as precursor for the stepwise elimination of CO via collision induced dissociation (CID). The recorded spectra reveal several bands which shift by reduction of the CO coverage. This hints at an according change of coordination motif. DFT calculations help to elucidate the effects of the decreasing CO coverage on the structure and the spin multiplicity of the complex. We will discuss first data of a mixed CO-N₂ complex [Co₄(CO)₈(N₂)₁(dppa-H⁺)]⁻.

[1] J. Mohrbach et al., J. Mol. Spectrosc., 2016 (accepted)

[2] C. Moreno et al., J. Organomet. Chem., 1993, 452, 185

MO 4.3 Mon 17:30 N 25

Multi-spectroscopic analyses of diphenyl ether complexes with tert-butyl alcohol and water in the electronic ground and excited state — ●DOMINIC BERNHARD¹, FABIAN DIETRICH¹, MARIYAM FATIMA², ANJA POBLOTZKI³, MARTIN SUHM³, MELANIE SCHNELL², and MARKUS GERHARDS¹ — ¹Fachbereich Chemie, TU Kaiserslautern — ²MPI für Struktur und Dynamik der Materie, Hamburg — ³Institut für Physikalische Chemie, Universität Göttingen

Diphenyl ether (DPE) represents a system with competing docking sites for alcohols leading to OH-O and OH-π structures. Recently the DPE – methanol complex was investigated in a multi-spectroscopic work in the electronic ground state (S₀) where a dominating OH-π structure was found in agreement with theory. In the electronically excited state (S₁) the OH-π interaction is strengthened which was revealed in a combined IR/UV spectroscopic and theoretical work. Starting from these findings complexes of DPE with tert-butyl alcohol and

water are investigated which are supposed to be completely different dispersion energy donors. For both complexes FTIR, microwave and mass- and isomer-selective IR/R2PI spectra were recorded revealing two co-existing OH-O and OH- π isomers in the S_0 state which are surprisingly in *both* cases predicted to be almost equally stable. In the S_1 state of DPE – *tert*-butyl alcohol vibrational spectra could be recorded separately for both isomers using UV/IR/UV spectroscopy; a retention of each structural motif is obtained, but the OH-O bond is weakened for the OH-O arrangement and the OH- π interaction is strengthened in the case of the OH- π isomer.

MO 4.4 Mon 17:45 N 25

[B₁₂Cl₁₁]⁻: An anionic superelectrophile? — MARKUS ROHDENBURG¹, MARTIN MAYER², MAX GRELLMANN², CARSTEN JENNE³, TOBIAS BORRMANN¹, FLORIAN KLEEMISS⁴, VLADIMIR A. AZOV¹, KNUT R. ASMIS², SIMON GRABOWSKY⁴, and JONAS WARNEKE⁵ — ¹University of Bremen, Institute of Applied and Physical Chemistry — ²Wilhelm-Ostwald-Institut für Physikalische und Theoretische Chemie, Universität Leipzig — ³Bergische Universität Wuppertal, Fakultät für Mathematik und Naturwissenschaften — ⁴University of Bremen, Institute of Inorganic Chemistry and Crystallography — ⁵Physical Science Division, Pacific Northwest National Laboratory, USA

Noble-gas (Ng) binding at room temperature is characteristic of super-electrophilic dications. Here, we report on the binding of krypton and xenon by the closo-dodecaborate anion [B₁₂Cl₁₁]⁻. The [B₁₂Cl₁₁Ng]⁻ complexes are thermodynamically stable species with Ng binding energies of 80 to 100 kJ/mol and contain B-Ng bonds with a significant degree of covalent interaction. The electrophilic nature of the boron binding site in [B₁₂Cl₁₁]⁻ is spectroscopically confirmed by the observation of a blue shift of the CO stretching mode in [B₁₂Cl₁₁CO]⁻. The characteristic electric field in front of the reactive site of [B₁₂Cl₁₁]⁻ results in a barrier for polar molecules, promoting the formation of Ng-complexes that are not detected with reactive cations like C₆H₅⁺. This introduces the new chemistry of "dipole discriminating electrophilic anions". Implications for noble gas compounds and the fundamental concept of electrophilicity are discussed.

MO 4.5 Mon 18:00 N 25

Optical photodissociation spectroscopy of metal lumichrome ionic complexes using the 22-Pole BerlinTrap — DAVID MÜLLER, PABLO NIETO, ALAN GÜNTHER, ALEX SHELDRIK, and OTTO DOPFER — Institut für Optik und Atomare Physik, Technische Universität Berlin, Hardenbergstr. 36, 10623 Berlin

Flavin-containing systems act as light sensors in plants and as blue-light receptors in fungi due to their wide spectral absorption from the VIS to the UV. They differ in their substituents at the N10 position. The simplest flavin without any substituent is lumichrome (LC). Most experiments concerning flavins were performed in solution, but not on isolated gas phase ions. Hence, the influence of the solvent and the ions is not fully understood yet. We report first vibronic spectra of protonated lumichrome H⁺LC [1] and metalated lumichrome (M⁺LC, M = Li-Cs). The gas-phase ions are generated in an ESI-source, mass-selected by a QPMS and cooled in a cryogenic 22-pole trap. After laser irradiation (380-500 nm) the fragments are mass-selected by an orthogonal ReTOF mass spectrometer. This design enables us to detect all fragments and the parent ion simultaneously. By comparison to quantum chemical calculations, we can assign the N5 position as the protonation site and the O4 position as the metalation site.

[1] A. Günther et al., J. Mol. Spectrosc. (2016), in press DOI:10.1016/j.jms.2016.08.017

MO 4.6 Mon 18:15 N 25

Vibrational Blue Shift of coordinated N₂ in [Fe₃O(OAc)₆(N₂)_n]⁺: "Non Classical" Dinitrogen Complexes — JOHANNES LANG, JENNIFER MOHRBACH, SEBASTIAN DILLINGER, JOACHIM HEWER, and GEREON NIEDNER-SCHATTEBURG — Fachbere-

ich Chemie und Forschungszentrum OPTIMAS, Technische Universität Kaiserslautern, 67663 Kaiserslautern, Germany.

The discovery of transition metal dinitrogen complexes in 1965 launched the ever growing research field of N₂ coordination chemistry. Spectroscopically, metal-N₂ bonding manifests itself by shifted N₂ stretching vibration frequencies in relation to the (IR inactive) frequency of the free N₂ molecule. Predominantly, N₂ complexes exhibit vibrational red shifts [1,2], which is well understood in terms of the Dewar-Chatt-Duncanson (DCD) model [3].

Here, we present "non classical" dinitrogen complexes [Fe₃O(OAc)₆(N₂)_n]⁺ (n = 1,2,3) in the gas phase at cryo temperatures. Infrared photo dissociation (IR-PD) as well as density functional theory (DFT) calculations reveal blue shifted N₂ stretching vibration bands. A detailed analysis of the electronic and steric interplay between N₂ and the [Fe₃O(OAc)₆]⁺ unit indicates strengthened N-N bonds due to pronounced σ bonding and a lack of π back donation.

[1] S. Dillinger, J. Mohrbach, J. Hower, M. Gaffga, G. Niedner-Schatteburg, PCCP 2015, 17, 10358-10362.

[2] F. Studt, F. Tuczek, J. Comp. Chem. 2006, 27, 1278-1291.

[3] G. Frenking and N. Fröhlich, Chem. Rev., 2000, 100, 717-774.

MO 4.7 Mon 18:30 N 25

High density source for slow and internally cold polar molecules reaching a collision limited regime — THOMAS GANTNER, MANUEL KOLLER, XING WU, SOTIR CHERVENKOV, MARTIN ZEPPEFELD, and GERHARD REMPE — Max-Planck-Institut für Quantenoptik, 85748 Garching, Germany

We present a new source for intense beams of slow and internally cold polyatomic molecules. By employing buffer gas cooling, an intense beam of molecules is achieved, reaching a single state purity of up to 92% [1]. Subsequently, the molecules are decelerated by a centrifuge decelerator [2] to a kinetic energy corresponding to less than 1 K. This combination produces cold guided molecules at fluxes exceeding 10¹⁰/s and densities of over 10⁹/cm³. We thereby enter a regime where cold dipolar collisions can be observed directly in a quadrupole guide. Utilizing the technique for a range of molecules (ND₃, CH₃F, CHF₃, CF₃CCH, CH₃OH, and C₃H₇OH) demonstrates its wide applicability.

[1] X. Wu et al., ChemPhysChem 2016, 17, 3631

[2] S. Chervenkov et al., Phys. Rev. Lett. 112, 013001 (2014)

MO 4.8 Mon 18:45 N 25

Characterising and Optimising of a Novel Laser Desorption Source — NICOLE TESCHMIT^{1,2}, DANIEL HORKE^{1,2}, KAROL DŁUGOŁĘCKI¹, DANIEL GUSA¹, and JOCHEN KÜPPER^{1,2,3} — ¹Center for Free-Electron Laser Science, DESY, Hamburg — ²The Hamburg Center for Ultrafast Imaging, University of Hamburg — ³Department of Physics, University of Hamburg

The control of small and moderate-size gas-phase molecules, such as the spatial separation of different quantum states, conformers, and molecular clusters, has been demonstrated, using static and/or dynamic electric fields [1]. Here, we present a new laser-desorption source for the production of very cold molecular beams, which will extend the above-mentioned techniques to larger biologically important molecules, such as peptides. The molecular beam of a laser-desorption source is for the first time characterized using strong field ionization by a femtosecond laser, combined with a time of flight mass spectrometer. Strong field ionization allows the detection of all existing species (including molecular fragments produced by the desorption process) and atoms in the interaction region. The beam can now be fully characterized and the conditions optimized for the production of intact sample molecules in the beam and the separation of one conformer from the beam can be shown. This makes this source suitable for use with non-species selective techniques, like time resolved single molecule diffractive imaging experiments.

[1] Y.-P. Chang, D. A. Horke, S. Trippel, J. Küpper, Int. Rev. Phys. Chem. 34, 557 (2015)

MO 5: Clusters I (with A)

Time: Tuesday 11:00–13:00

Location: N 6

Invited Talk

MO 5.1 Tue 11:00 N 6

Cryo Kinetics and Spectroscopy of 3d Metal Clusters and Alloys — JENNIFER MOHRBACH, SEBASTIAN DILLINGER, MATTHIAS KLEIN, AMELIE EHRLHARD, and ●GEREON NIEDNER-SCHATTEBURG — Fachbereich Chemie, TU Kaiserslautern

The cluster surface analogy motivates us to utilize our hybrid tandem ion trap instrument (cryo-RF-hexapole and cryo-FT-ICR trap) for the study of adsorption and reaction kinetics of clusters under single collision conditions at 11–30 K, and for IR Photon Dissociation (IR-PD) spectroscopy initially focusing on the one and two colour investigations of metal organic complexes^[1] and lately extended towards their N₂ adsorption properties^[2].

We have started a systematic study of N₂ and H₂ cryo adsorption on size selected Fe, Co, and Ni clusters, and their alloys^[3]. Adsorption kinetics show mono layer like adsorbate shells. IR-PD spectra of cluster adsorbate complexes [M_n(N₂)_m]⁺ reveal complex patterns – DFT modelling providing some support. There are adsorbate coverage dependent spectral shifts and splittings that report on the cluster and adsorbate geometries. We compare to our synchrotron X-ray based studies of spin and orbital contributions to the total magnetic moments of the clusters^[4]. Supported by SFB 3MET.de.

[1] Y. Nosenko et al. PCCP **15**, 8171 (2013); J. Lang et al. PCCP **16**, 17417 (2014). [2] J. Lang et al., Chem.Comm 2016 (in print). [3] S. Dillinger et al. PCCP **17**, 10358 (2015); J. Mohrbach et al. JPC A 2016 (submitted). [4] S. Peredkov et al. PRL **107**, 233401 (2011); J. Meyer et al. JCP **143**, 104302 (2015)

MO 5.2 Tue 11:30 N 6

Unusual magic numbers in Si_n⁺-Ar_m clusters — ●MARKO FÖRSTEL, BERTRAM JAEGER, PHILIPP SPORKHORST, and OTTO DOPFER — Institut für Optik und Atomare Physik, Technische Universität Berlin, Hardenbergstrasse 36, D-10623 Berlin

Silicon ions are found in the interstellar medium and in Earth's atmosphere. They are also involved in semiconductor manufacturing processes. The fundamental chemistry, behavior, and structure of Si_n⁺ ions are, however, still poorly understood. Here we probe the anisotropic electronic structure of the Si_n⁺ ion in form of the Si_n⁺-Ar_m potential energy surface by using argon ligands. Si_n⁺-Ar_m clusters are produced in a laser vaporization source and then analyzed in a mass spectrometer. Depending on the cluster source conditions we observe unusual magic numbers that cannot be explained satisfyingly by assuming an icosahedric argon shell. We interpret our observations as an effect of the strong anisotropy in the interaction potential of the Si⁺ ion caused by its unpaired electron. We present the observed magic numbers of Si_n⁺-Ar_m clusters and discuss the underlying structures with the help of quantum chemical calculations.

MO 5.3 Tue 11:45 N 6

Absorption of diamondoid-noble metal cluster hybrids studied with ion yield spectroscopy — ●TOBIAS BISCHOFF¹, ANDRE KNECHT¹, ANDREA MERLI¹, VICENTE ZAMUDIO-BAYER², TOBIAS LAU³, BERND VON ISSENDORFF², MERLE RÖHR⁴, JENS PETERSEN⁴, ROLAND MITRIC⁴, THOMAS MÖLLER¹, and TORBJÖRN RANDER¹ — ¹TU Berlin, Germany — ²U Freiburg, Germany — ³Helmholtz-Zentrum Berlin, Germany — ⁴U Würzburg, Germany

The study of the radiative emission rate enhancement of molecules near metal surfaces has led to important applications such as single molecule spectroscopy. While interaction-induced amplification rates as high as 14 orders of magnitude have been already observed, there is still debate about the fundamental processes responsible for the enhancement. On the molecular size scale, small metal clusters may be used to systematically study the interaction between a metal subunit and a fluorophore. Diamondoids, perfectly shape and mass selected sp³ hybridized nanodiamonds, show intrinsic luminescence and can be selectively functionalized. We were able to synthesize hybrid systems of diamondoids and small metal cluster cations in the gas phase. This approach enables us to study the optical properties of tailored hybrid systems. Here, we present the UV/VIS absorption of adamantanethiol-Au₃/Ag₃ hybrid systems, measured through ion yield spectroscopy. An analysis of both the hybrid and single subunit absorptions shows significant differences in spectral composition depending on the type of metal cluster. We attribute these differences to charge transfer states

in the hybrid systems.

MO 5.4 Tue 12:00 N 6

Disentangling water cluster beams — ●HELEN BIEKER^{1,2}, DANIEL HORKE^{1,2}, DANIEL GUSA¹, BORIS SARTAKOV³, ANDREY YACHMENEV¹, and JOCHEN KÜPPER^{1,2,4} — ¹Center for Free-Electron Laser Science, DESY — ²The Hamburg Center for Ultrafast Imaging, University of Hamburg — ³General Physics Institute, Russian Academy of Sciences — ⁴Department of Physics, University of Hamburg

To unravel the microscopic details of intermolecular interactions in water, we prepare controlled samples of size- and isomer-selected water clusters. Inhomogeneous electric fields allow us to create pure samples of individual structural isomers or of size-selected molecular clusters and to disperse molecules in a beam according to their quantum states [1].

Here, we aim to develop an understanding of the structures of water clusters containing a few monomer units. We present our first results on the production of size-selected samples using supersonic expansions, subsequent dispersion of the various clusters in strong electric fields, extending previous studies [2]. We introduce a simple theoretical description of water dimer in an electric field. Future experiments aim at utilizing x-ray and electron diffractive imaging to study the structures and ultrafast dissociation dynamics of these polymolecular systems.

[1] Y.P. Chang, D. A. Horke, S. Trippel and J. Küpper, *Int. Rev. Phys. Chem.* **34**, 557-590 (2015)

[2] R. Moro, R. Rabinovitch, C. Xia, and V.V. Kresin, *Phys. Rev. Lett.* **97**, 123401 (2006)

MO 5.5 Tue 12:15 N 6

D-Dimensional Fourier Grid Hamiltonian Method with Potential-Adapted Grid for Hydrogen Isotopologue Cluster Computations — ●ALEXANDER KRAUS, ROBIN GRÖSSLE, and SEBASTIAN MIRZ — Karlsruhe Institute of Technology, Institute for Technical Physics, Tritium Laboratory Karlsruhe

In order to determine the systematic effect of molecular hydrogen clusters on the neutrino mass measurement with KATRIN, a computational method is needed that can be used for a calculation of initial and final beta decay states.

For this purpose, the Fourier Grid Hamiltonian Method has been generalized to *d* dimensions. A grid generation algorithm has been introduced that chooses sparse sampling points which represent the potential sufficiently to save computation time. The *d*-dimensional inverse FFT is used for fast computation of matrix elements. Eigenvalues and Eigenstates are approximated by parallel Lanczos diagonalization.

An overview of the constructed algorithm is given and first results and benchmarks are shown in this talk.

This method could also be useful to infrared spectroscopy of liquid hydrogen isotopologues for a better quantitative understanding of cluster excitations.

MO 5.6 Tue 12:30 N 6

Highly nonlinear optical response of organotin cluster molecules — ●NILS W. ROSEMAN^{1,3}, JENS P. EUSSNER², ANDREAS BEYER³, STEPHAN W. KOCH³, KERSTIN VOLZ³, STEFANIE DEHNEN², and SANGAM CHATTERJEE¹ — ¹Institute of Experimental Physics I, Justus-Liebig-Universität Giessen, Heinrich-Buff Ring 16, D-35392 Giessen, Germany — ²Faculty of Chemistry and Materials Sciences Center, Philipps-Universität Marburg, Hans-Meerwein-Straße, D-35043 Marburg, Germany — ³Faculty of Physics and Materials Science Center, Philipps-Universität Marburg, Renthof 5, D-35032 Marburg, Germany

Organotin-based cluster molecules exhibit a large variety of physical properties. These depend on the clusters chemical composition as well as the spatial arrangement of the constituents. Variation of these two parameters usually results in highly complex electronic landscapes. Consequently, such cluster molecules exhibit a very specific linear response and ultimately nonlinear optical properties.

Here, we present the extreme nonlinear optical response of a cluster molecule composed of a SnS cluster-core decorated with styryl-ligands. The ligands, on the one hand, prevent crystallization and provide delocalized electrons that are responsible for the nonlinear response on

the other hand. These peculiarities result in low-threshold white-light generation. The latter is simulated numerically using an anharmonic oscillator model and experimental parameters only.

MO 5.7 Tue 12:45 N 6

Infrared spectra and structures of boron-doped silicon clusters — •BERTRAM KLAUS AUGUST JAEGER¹, NGUYEN XUAN TRUONG¹, SANDY GEWINNER², WIELAND SCHÖLLKOPF², ANDRE FIELICKE¹, and OTTO DOPFER¹ — ¹IOAP, TU Berlin, Germany — ²FHI, Berlin, Germany

Silicon-based nanostructures have gained interest for nanoelectronics and nanophotonics. Therefore, the investigation of controlled change

of physical and chemical properties of silicon clusters by doping will aid in developing novel cluster-containing nanostructures. Here we study neutral silicon-rich silicon-boron clusters (Si_nB_m , $n=3-8$, $m=1-2$) via mass spectrometry, resonant infrared-ultraviolet two-color ionization (IR-UV2CI) spectroscopy and quantum chemical calculations [1]. The most stable isomers are found utilizing global energy optimization. Their linear IR absorption spectra are compared to the IR-UV2CI spectra, thus determining the geometries of the observed Si_nB_m clusters. Different physical properties such as charge distributions, ionization energies and bond energies will be discussed. As the B-B bond is stronger than the B-Si and Si-Si bonds, boron segregation is observed for Si_nB_m clusters with $m=2$.

[1] N.X. Truong et al., Int. J. Mass Spectrom., 2016, 395, 1-6

MO 6: Theory of Molecular Dynamics

Time: Tuesday 11:00–12:45

Location: N 25

Invited Talk

MO 6.1 Tue 11:00 N 25

Illuminating Molecular Symmetries with Bicircular High-Order-Harmonic Generation — •DANIEL M. REICH^{1,2} and LARS BOJER MADSEN¹ — ¹Department of Physics and Astronomy, Aarhus University, DK-8000 Aarhus C, Denmark — ²Theoretische Physik, Universität Kassel, Heinrich-Plett-Straße 40, 34132 Kassel, Germany

High-order-harmonic generation (HHG) represents one of the primary gateways towards obtaining novel tabletop light sources with unique properties for a wide range of applications. In this work we present a general theory of bicircular HHG from N-fold rotationally symmetric molecules.

Using a rotating frame of reference we predict the complete structure of the high-order-harmonic spectra for arbitrary driving frequency ratios and show how molecular symmetries can be directly identified from the harmonic signal. Our findings reveal that a characteristic fingerprint of rotational molecular symmetries can be universally observed in the ultrafast response of molecules to strong bicircular fields pointing towards the possibility of ultrafast readout of molecular symmetries in, e.g., chemical reactions.

MO 6.2 Tue 11:30 N 25

Interference stabilization for discrete states coupled to a number of continua — •NICOLA MAYER, OLEG KORNILOV, and MISHA IVANOV — Max Born Institute, Max-Born-Straße 2A, 12489 Berlin, Germany

When two discrete states coupled to a common continuum overlap in energy, a counterintuitive quantum mechanical effect, commonly known as interference stabilization [1] or interference narrowing, manifests itself by stabilizing one of the two states as the coupling strength to the continuum increases. The effect was first proposed and studied for laser-dressed Rydberg states. In our recent work we demonstrated that interference stabilization also takes place in auto-ionizing states of N₂ molecule using a time- and angular-resolved photoelectron spectroscopy experiment [2] [3]. Here we generalize the theory of Ref. [3] for an arbitrary number of continua coupled to two states and tackle the problem of three or more states coupled to two or more continua, drawing analogies with the Stimulated Raman Adiabatic Passage (STIRAP) effect, in search for possible geometric-phase-induced effects on the populations of the states.

Reference:

[1] M.V. Fedorov, Atomic and free electrons in a strong light field. World Scientific, 1998.

[2] M. Eckstein, et al., Phys. Rev. Lett., 116, 153003, 2016.

[3] M. Eckstein, N. Mayer et al., Faraday Discuss., DOI: 10.1039/C6FD00093B, 2016.

MO 6.3 Tue 11:45 N 25

Non-Hermitian Surface Hopping — •XING GAO¹ and WALTER THIEL² — ¹Max-Planck-Institut für Physik komplexer Systeme — ²Max-Planck-Institut für Kohlenforschung

It is quite a challenge to balance coherence and decoherence effects in non-adiabatic mixed quantum-classical dynamics such as Ehrenfest and surface hopping dynamics. Here we address this challenge by presenting a generalized non-Hermitian equation of motion (nH-EOM) which is derived using the Born-Huang expansion of the total wavefunction and the polar representation of the nuclear factor. Com-

pared to standard trajectory surface hopping, the nH-EOM contains two additional terms, a skew symmetry term $i\Gamma$ with dissipation operator Γ to account for decoherence and a renormalized kinetic-energy term to take care of phase shifts, without destroying the invariance to the choice of representation. Numerically, the nH-EOM can still be solved efficiently using a semiclassical approximation in the framework of Tully's fewest-switches surface hopping (FSSH) algorithm. Applications to molecular collision model Hamiltonians demonstrate improved performance over the standard FSSH approach, through comparison to exact quantum results.

MO 6.4 Tue 12:00 N 25

Current density calculation using quantum hydrodynamics approach — •TAMADUR ALBARAGHTEH, KLAUS RENZIEHAUSEN, and INGO BARTH — Max Planck Institute of Microstructure Physics, Weinberg 2, 06120 Halle (Saale), Germany

The inability of the Born-Oppenheimer approximation (BO) to predict accurately electron current densities for dynamics of molecular vibronic wave packets in a single electronic state is a well-known problem [1]. These electron current densities vanish incorrectly within the BO approximation. However, the electron current density is one of the important quantities that characterize the electron motion. Quantum hydrodynamics (QHD) approach has turned out to be the most convenient approach to overcome the BO failure. This approach provides a way to calculate non-zero electron current densities. In this work, one free particle described by a Gaussian wavepacket is used as a test system for the calculation of the current density and other quantities. Our QHD approach to calculate these quantities is to solve the Ehrenfest equation of motion numerically using modern numerical methods, based on computational fluid dynamics (CFD) [2]. The numerical results of different quantities of the system show good agreement with corresponding analytic results. Moreover, we plan to calculate the electron current density of the vibrating H_2^+ molecule in a single electronic BO state.

[1] I. Barth et al., Chem. Phys. Lett. 481, 118 (2009)

[2] R. J. Leveque, Finite Volume Methods for Hyperbolic Problems, Cambridge University Press, Cambridge (2004)

MO 6.5 Tue 12:15 N 25

Electron-nuclear wave-packet dynamics through a conical intersection: does the electron care? — •JULIAN ALBERT¹, KILIAN HADER¹, E. K.U. GROSS², and VOLKER ENGEL¹ — ¹Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Emil-Fischer-Str. 42, 97074 Würzburg, Germany — ²Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, 06120 Halle, Germany

We investigate the coupled electron-nuclear dynamics in a model system showing a conical intersection (CoIn) between two excited state potential energy surfaces. Within the model, a single electron and nucleus move in two dimensions in an external static field. It is demonstrated that the nuclear density conserves its initial Gaussian shape when passing the CoIn whereas the electronic density remains approximately constant. This is in sharp contrast to the picture which evolves from an analysis within the basis of adiabatic electronic states. There, dramatic changes are seen in the dynamics of the different nuclear components of the total wave function. It is thus documented that neither the nuclear nor the electronic density obtained directly from the wave packet motion in the complete configuration space spanned

by electronic and nuclear degrees of freedom, are influenced by the existence of a CoIn.

MO 6.6 Tue 12:30 N 25

Coupled electron-nuclear dynamics: A comparison of methods and dimensionality — •THOMAS SCHNAPPINGER, JULIUS ZAULECK, ROBERT SIEMERING, and REGINA DE VIVIE-RIEDLE — Department Chemie, LMU München

The purpose of this work is a first comparison of two methods describing a coupled electron-nuclear dynamics: the purely quantum mechanical ansatz NEMol and the TD-DFT based Ehrenfest dynamics. For this purpose the dynamics of (Z)-3-aminoacrolein in the electronic

ground state was analyzed. Using different quantum chemical methods the potential profile of tautomerism was calculated and the critical points of the reaction were identified to set up one-dimensional potential energy surfaces along the reaction.

We introduce a novel form of the NEMol ansatz which is formulated for a single electronic state. Using the one-dimensional potential energy surfaces of the tautomerism we are able to calculate the coupled electron-nuclear dynamic.

The comparison between the NEMol ansatz and the TD-DFT Ehrenfest dynamics is so far limited due to the difference in dimensionality. Therefore an approach for one-dimensional TD-DFT Ehrenfest dynamics is presented. In addition a short outlook is provided how to select and evaluate the chosen dimensions for a dynamic simulation.

MO 7: Helium Droplets and Systems (with A)

Time: Tuesday 14:30–16:15

Location: N 6

Invited Talk

MO 7.1 Tue 14:30 N 6

Cluster Studies with the BerlinTrap — •PABLO NIETO, ALAN GÜNTHER, DAVID MÜLLER, ALEX SHELDRIK, and OTTO DOPFER — Institut für Optik und Atomare Physik, Technische Universität Berlin, Hardenbergstr. 36, D-10623 Berlin, Germany

The first experiments using a novel tandem mass spectrometer (BerlinTrap) which combines an electrospray ion source, a quadrupole mass spectrometer, a cryogenic 22-pole ion trap (4-300 K), and an orthogonal reflectron time-of-flight mass spectrometer [1] are presented. First, the generation of small He clusters around cold metal ions (He_nM^{q+}) by successive aggregation of He atoms is presented. The attraction between a positive charge and the surrounding He leads to the formation of a shell of strongly bonded atoms around the ion often called snowball. The study of He snowballs has been carried out in the last years by photo- or electron impact ionization of the atom or molecule embedded in relatively large He droplets. This study constitutes the first bottom-up approach to the formation of He snowballs around an ion using a gentle growth scheme. The formation of some clusters with a given (magic) number of He atoms is greatly enhanced signaling a high relative stability. In the second part of the talk structure and optical absorption properties of metalated flavins in the gas phase are discussed. The present results illustrate the broad variety of atomic and molecular ionic clusters which can be studied with the BerlinTrap by mass spectrometry and spectroscopy.

[1] A. Günther, P. Nieto, D. Müller, A. Sheldrick, D. Gerlich, and O. Dopfer, *J. Mol. Spectrosc.*, in press, DOI:10.1016/j.jms.2016.08.017

MO 7.2 Tue 15:00 N 6

Libration of strongly-oriented polar molecules inside a superfluid — •ELENA REDCHENKO and MIKHAIL LEMESHKO — IST Austria (Institute of Science and Technology Austria), Am Campus 1, 3400 Klosterneuburg, Austria

Recently, it was shown that molecular rotation inside a superfluid, such as a helium nanodroplet or a Bose-Einstein condensate, leads to formation of a quasiparticle of a new kind – the angulon. The angulon represents a quantum rotor dressed by a field of many-particle excitations. In this work, we demonstrate that in the strong-field limit the angulon turns into the ‘pendulon’ – a quantum spherical liblator, whose pendular motion is altered by the field of phonon excitations, and study the properties of the pendulon quasiparticle. We have shown that an electric field relaxes the selection rules on the angular momentum exchange between the molecule and the bath, which results in a series of instabilities absent in the field-free case of the angulon quasiparticle. In other words, a field renders the instabilities universal, i.e. independent on the details of the molecule-boson potential energy surface. Furthermore, a field acts as an additional knob for altering the positions of the instabilities in the molecular rotational spectrum, thereby opening the door for detailed experimental studies of redistribution of orbital angular momentum in many-particle systems.

[1] Redchenko E.S., Lemeshko M., *Chemphyschem.* 2016 Nov 18;17(22):3649-3654.

MO 7.3 Tue 15:15 N 6

Fingerprints of the angulon quasiparticle in spectra of molecules in superfluid helium droplets — •IGOR CHEREPANOV and MIKHAIL LEMESHKO — Institute of Science and Technology Austria (IST Austria), Am Campus 1, 3400 Klosterneuburg, Austria

The recently developed angulon theory [1] represents a powerful tool to study interactions between a rotating molecular impurity and a macroscopically large number of helium atoms in a superfluid helium nanodroplet. The comparison of the experimental data on the renormalization of rotational constants for a wide range of different molecules and the predictions of the angulon theory [2] provides a strong evidence for angulon formation in superfluid ^4He .

Here we demonstrate that angulon theory is also able to explain some features observed in the ro-vibrational spectra of the ν_3 band of the methyl radical [3] and the ammonia molecule [4] solvated in superfluid ^4He . We found that one of the largest anisotropic terms in the $\text{CH}_3(\text{NH}_3)\text{-He}$ potential expansion induces a transfer of one quantum of angular momentum from the molecule to the many-body bath. As a consequence, the spectral line corresponding to the $^R\text{R}_1(1)$ transition becomes significantly broadened and suppressed compared to the gas phase. This amounts to an experimental confirmation of the angulon instabilities, recently predicted in Ref. [1].

[1] R. Schmidt, M. Lemeshko, *Phys. Rev. Lett.* **114**, 203001 (2015)

[2] M. Lemeshko, arXiv:1610.04908 (2016)

[3] A. Morrison et al., *J. Phys. Chem. A* **117**, 11640 (2013)

[4] M. Slipchenko, A. Vilesov, *Chem. Phys. Lett.* **412**, 176 (2005)

MO 7.4 Tue 15:30 N 6

Gold doped helium nanodroplets: Electronic spectroscopy from atoms to nanoparticles — •FLORIAN LACKNER, MAXIMILIAN LASSERUS, ROMAN MESSNER, MARTIN SCHNEDLITZ, ALEXANDER VOLK, PHILIPP THALER, and WOLFGANG E. ERNST — Institute of Experimental Physics, TU Graz

The isolation of nanoparticles in helium nanodroplets offers low temperature confinement for a dopand size regime ranging from single atoms and molecules to large clusters and elongated wire-structures. Excitation spectra of gold atoms, residing inside the droplets, appear strongly blue shifted due to the repulsive Pauli interaction of excited electrons with the He environment. Consequently, for the $5d^{10}6p\ ^2P_{1/2}^o \leftarrow 5d^{10}6s\ ^2S_{1/2}$ transition in Au-He_N we observe a broad structure extending more than 800 cm^{-1} to the blue of the bare atom line located at $37,359\text{ cm}^{-1}$. This feature is superimposed by a peak around $37,950\text{ cm}^{-1}$ attributed to atoms that have relaxed into the $5d^96s^2\ ^2D$ manifold, a pathway enabled by the droplet environment and forbidden in the free atom. Absorption spectra of larger nanoparticles can be recorded ex-situ after deposition on fused silica substrates. First results on Au nanoparticles prepared by helium nanodroplets show a characteristic surface plasmon resonance peaking around 530 nm. We expect that the formidable doping capabilities provided by helium nanodroplets will allow for the study of the electronic structure of a large variety of mono- and bi-metallic nanoparticles ranging from single atoms and molecules to large nanoparticles.

MO 7.5 Tue 15:45 N 6

Far-Infrared Spectroscopy of Molecules and Aggregates in Helium Nanodroplets at FELIX — •GERHARD SCHWAAB¹, RAFAEL SCHWAN¹, DEVENDRA MANI¹, NITISH PAL¹, BRITTA REDLICH², LEX VAN DER MEER², and MARTINA HAVENITH¹ — ¹Physikalische Chemie 2, Ruhr-Universität Bochum — ²FELIX Laboratory, Radboud University Nijmegen

Helium nanodroplets provide the opportunity to study molecules and

molecular aggregates at temperatures of 0.37 K in a suprafluid matrix. Recently we have moved one of our helium droplet machines to the free electron laser facility FELIX in Nijmegen. First test molecules included SF₆, water, water clusters and water-HCl clusters.

The high output energy and broad frequency coverage of the FELIX I and FELIX II beamlines allows access to the low frequency ($\nu > 100\text{ cm}^{-1}$) far-infrared range in spite of the low energy per photon. Especially the spectrum of small water clusters in this region is astonishingly rich. An overview of the experimental setup and the results of our latest micro-solvation studies will be given.

MO 7.6 Tue 16:00 N 6

Infrared spectroscopy of HCl dissociation at 0.37K using free electron lasers. — ●DEVENDRA MANI¹, RAFFAEL SCHWAN¹, THEO FISCHER¹, ARGHYA DEY^{1,2}, MATIN KAUFMANN¹, BRITTA REDLICH², LEX VAN DER MEER², GERHARD SCHWAAB¹, and MARTINA HAVENITH¹ — ¹Lehrstuhl für Physikalische Chemie II, Ruhr Universität Bochum, Germany. — ²Institute for Molecules and Materials (IMM), Radboud University Nijmegen, Nijmegen, Netherlands

Dissociation of HCl in presence of few water molecules has recently been studied theoretically as well as spectroscopically. [1,2] These studies suggest that 4 water molecules are sufficient to dissociate one HCl molecule, forming a solvent separated $\text{H}_3\text{O}^+(\text{H}_2\text{O})_3\text{Cl}^-$ dissociated cluster. Until now, attempts to observe this dissociated species had been focused on the O-H and H-Cl stretch regions. However, the results were obscured by the presence of vibrational bands of different $(\text{HCl})_m - (\text{H}_2\text{O})_n$ undissociated clusters in this spectral range. From the recent theoretical calculations [3], the umbrella type motion of the H_3O^+ moiety (prediction: broad band, $1300\text{--}1360\text{ cm}^{-1}$) appears to be a fingerprint signature for the dissociated cluster. We have studied this dissociation reaction in helium droplets, in the frequency range of $900\text{--}1700\text{ cm}^{-1}$, using free electron lasers at FELIX. A weak broad band, spanning from 1000 to 1450 cm^{-1} , could be observed on specific mass channels. The results will be discussed in detail in the talk.

References: 1) H. Forbert et al., J. Am. Chem. Soc., **133**, 4062 (2011). 2) A. Gutberlet et al., Science, **324**, 1545 (2009). 3) J. M. Bowman et al., Phys. Chem. Chem. Phys., **17**, 6222 (2015).

MO 8: Fast Intramolecular Dynamics

Time: Tuesday 14:30–16:30

Location: N 25

Invited Talk

MO 8.1 Tue 14:30 N 25

Ultrafast dynamics of a magnetically bistable molecular switch by fs transient absorption spectroscopy — ●SEBASTIAN MEGOW¹, JULIA BAHRENBURG¹, HENDRIK BÖHNKE¹, MATS BOHNSACK¹, MARK DITTNER¹, MARCEL DOMMASCHK², RAINER HERGES², and FRIEDRICH TEMPS¹ — ¹Institute of Physical Chemistry, Christian-Albrechts-University, Max-Eyth-Strasse 1, 24098 Kiel, Germany — ²Otto-Diels-Institute of Organic Chemistry, Christian-Albrechts-University, Otto-Hahn-Platz 6/7, 24098 Kiel, Germany

The phenylazopyridine(PAP)-functionalized Ni-porphyrin-based molecular switch, dubbed "record player" (RP), has recently drawn considerable attention as it shows magnetic bistability at room temperature in homogeneous solution upon irradiation [Venkataramani et al., Science **331** (2011)]. The reversible photoswitching process between the diamagnetic low- and the paramagnetic high-spin compound occurs under isomerization and (de-)coordination of the PAP moiety. Surprisingly, the spin-crossover seems to be triggered by absorption in the porphyrin macrocycle rather than photoisomerization of the PAP. To shed light on the underlying mechanism, we have monitored the ultrafast dynamics of the *cis*- and *trans*-PAP RP by means of fs transient absorption spectroscopy after photoexcitation. While the low-spin compound shows virtually identical dynamics to pure Ni-porphyrin without formation of any identifiable spin-switching product, the high-spin compound shows formation of the low-spin product within 12 ps with an estimated quantum yield of $6 \pm 1\%$.

MO 8.2 Tue 15:00 N 25

Time-Resolved Spectroscopy of the Molecular Rotor Thioflavin T and its Building Blocks — ●BASTIAN GEISSLER, PHILIPP GERSCHER, ANNA LISA SEMRAU, and PATRICK NUERNBERGER — Physikalische Chemie II, Ruhr-Universität Bochum, 44780 Bochum

Thioflavin T (ThT) is a benzothiazole salt linked to N,N-dimethylaniline. ThT is widely used as a marker for biophysical studies on the misfolding and aggregation of proteins. The spectroscopic properties of ThT depend on the freely rotatable bond between the benzothiazole and the aniline moieties. The associated rotation is the main (non-radiative) depopulation channel of the excited state, which has a lifetime well below 10 ps [1,2]. The fluorescence behavior of ThT exhibits a pronounced dependence on the excitation wavelength, attributed to the pre-rotation angle of the ground-state molecule [3].

We perform time-resolved spectroscopy via fluorescence upconversion, TCSPC and transient absorption for ThT and its building blocks. Depending on the excitation wavelength, fluorescence and excited-state dynamics drastically change, shifting from ps to ns. A comparison of ThT and benzothiazole confirms that for near-UV excitation, the ThT dynamics solely originate from a pre-rotated subensemble for which the two building blocks are spectroscopically independent and no excited-state depopulation through rotation occurs. Hence, our studies provide a time-domain corroboration of the pre-rotation model [3].

[1] V. Stsuapura et al., J. Phys. Chem. A **114**, 8345–8350 (2010).

[2] I. Kuznetsova et al., Anal. Chem. **88**, 718–724 (2016).

[3] S. Freire et al., Dyes Pigm. **110**, 97–105 (2014).

MO 8.3 Tue 15:15 N 25

Quantum chemical studies of a hemithioindigo-based photo-driven molecular motor — ●FLORIAN ROTT, SVEN OESTERLING, and REGINA DE VIVIE-RIEDLE — Department Chemie, LMU München

In recent years photodriven molecular motors got increasing interest due to their ability to convert light energy into directional motion and thus providing energies of future nanomachines.

Dube et al. [1] synthesised a hemithioindigo-based photodriven molecular motor. This motor performs a full rotation after excitation with visible light, showing $> 95\%$ unidirectionality at a very fast rate of 1 KHz at 20°C. The full rotation is believed to be a three step process consisting of two light induced and one thermal step.

However, the mechanism accounting for the rotation is not completely understood. To elucidate the reaction path we performed excited state quantum chemical calculations at the CASSCF level of theory. Several conical intersections are involved in the light-induced process and enables the fast rotation of the molecular motor.

[1] M. Guentner, M. Schildhauer, S. Thumser, P. Mayer, D. Stephenson, P. J. Mayer, H. Dube, Nat. Commun. **6**, 8406 (2015).

MO 8.4 Tue 15:30 N 25

Femtosecond dynamics of the 2-methylallyl radical in the gas phase — ●ANJA RÖDER¹, INGO FISCHER¹, ROLAND MITRIC¹, JENS PETERSEN¹, KEVIN ISSLER¹, MATTHIAS WOHLGEMUTH¹, and LIONEL POISSON² — ¹University of Wuerzburg, Am Hubland Süd 97074 Wuerzburg, Germany — ²LIDYL, CEA, CNRS, Université Paris-Saclay, CEA Saclay, F-91191 Gif-sur-Yvette, France

The methylated derivatives of the allyl radical (the 1-methylallyl or 2-methylallyl radical) are especially interesting for combustion chemistry, since biodiesel often contains branched or non-branched unsaturated fatty esters.

Produced via pyrolysis, the 2-methylallyl radical was examined using femtosecond pump-probe spectroscopy, with the pump laser wavelengths at 240 and 236 nm exciting into a p-state. The probe laser was the 800 nm fundamental of a Ti:Sapphire Laser. The lifetimes of these states were examined using time-resolved photoelectron spectroscopy (TRPES) or time-of-flight mass spectrometry (TOF-ms), showing two time-constants and considerable anisotropy in the photoelectron spectra.

Molecular-dynamic calculations using the field-induced surface hopping method coupled to DDFT reproduce well our experimentally result. The excited p-state decays faster than the time-resolution of the pump-laser to the 3s-state, which decays via the D1-state (first time constant) to the electronic ground state. (Second time constant) This assignment is further supported by the strong positive anisotropy in the photoelectron images, in agreement with ionization from an s-orbital.

MO 8.5 Tue 15:45 N 25

Time-resolved fluorescence studies of a polycyclic tetrazolium compound in solution — ●TOM BOLZE, JAN-LUCAS WREE, and PATRICK NUERNBERGER — Physikalische Chemie II, Ruhr-Universität Bochum, 44780 Bochum

Tetrazolium salts are usually colorless and non-fluorescent, whereas the closely related formazans exhibit a bright range of colors. Since reduction of tetrazolium compounds often leads to formazans, numerous applications have been developed that exploit the color change. However, also photo-oxidation can occur, so that e.g. phenyl-benzo[c]tetrazolo-cinnolinium (PTC), one of the very few known fluorescent tetrazolium compounds, is formed from triphenyl-tetrazolium chloride (TTC) upon irradiation with ultraviolet (UV) light in alcoholic solution.

We investigate the fluorescence dynamics of PTC using time-correlated single-photon counting (TCSPC) and femtosecond fluorescence upconversion. PTC is first generated photochemically by UV excitation of TTC at 265 nm. Our TCSPC results in ethanol disclose an excited-state lifetime of ≈ 700 ps for PTC after S_1 excitation and further indicate additional dynamics on an ultrafast time scale. As is evident in fluorescence upconversion measurements, these faster dynamics occur with a characteristic time constant of 6 ps for S_1 excitation, whereas this time constant is significantly longer for S_2 excitation, presumably reflecting the dissipation of different amounts of excess energy. Studies in more viscous solvents complement the results, and reaction pathways of excited PTC beyond the radiative one are discussed.

MO 8.6 Tue 16:00 N 25

Long-lived coherence with multiple vibrational frequencies in pentafluoropyridine as a probe of $\pi\pi^*$ - $\pi\sigma^*$ vibronic coupling — ●JONAS ANDREAS KUS, OLE HÜTER, and FRIEDRICH TEMPS — Institute of Physical Chemistry, Christian-Albrechts-University Kiel, Olshausenstraße 40, D-24098 Kiel, Germany

The electronic structure of pyridine changes significantly when the hydrogen atoms are substituted by fluorine. Due to the high electronegativity of fluorine, the $\pi\sigma^*$ state is energetically lowered. This so-called perfluoro effect enables vibronic coupling of the $\pi\sigma^*$ state with the lower-lying $\pi\pi^*$ state. Using femtosecond time-resolved time-of-flight mass spectrometry after excitation at $\lambda = 255$ nm, we observed multiple oscillations of the ion yield which can be attributed to the vibronic

coupling. A pronounced oscillation at a frequency around $\nu = 60$ cm $^{-1}$ is superimposed by several oscillations of higher frequency. From results of femtosecond photoelectron imaging spectroscopy, we can rule out population transfer from the initially excited $\pi\pi^*$ state to a different electronic state. Supported by quantum chemical calculations at the RI-SCS-CC2, CASSCF and XMCQDPT2 levels of theory, we suggest a strong distortion of the initially excited $\pi\pi^*$ state by the coupling to the higher-lying $\pi\sigma^*$ state. The wavepacket motion in the anharmonic double well potentials modulates the ionization probability, thereby causing the observed oscillations. Taking into account our recent result for pentafluorobenzene [Hüter *et al.*, JCP **145** (2016)], strong $\pi\pi^*$ - $\pi\sigma^*$ vibronic coupling seems to have an important general influence on the excited-state dynamics of perfluorinated aromatics.

MO 8.7 Tue 16:15 N 25

L_a or L_b , that is the question! – A quantum dynamical study of pyrene — ●MATTHIAS K. ROOS, SEBASTIAN REITER, and REGINA DE VIVIE-RIEDLE — Department Chemie, Ludwig-Maximilians-Universität München

Pyrene, the textbook example for the formation of excimers, is nowadays a widely used fluorescence marker, sensing molecule and building block in organic semiconductors useful for organic lightemitting diodes (OLEDs) or organic photovoltaic cells (OPV). Nonetheless, the basic mechanism behind its exceptional photophysics is not well understood.

Pyrene is excited by UV light to the S_2 state, a $\pi\pi^*$ state labeled L_a according to Platt's notation. Meanwhile, S_1 or L_b only has a negligible contribution to the absorption due to cancellation effects. Yet, emission occurs exclusively from the L_b state according to experiments. Therefore, an ultrafast relaxation pathway like a conical intersection between these two states must exist.

We use quantum dynamical methods to simulate this photophysical process on a two dimensional grid, built from displacement vectors between minimum structures. Therefore, we employ the Wilson G-Matrix method for the kinetic energy operator. The quantum chemical potential is dealt with a state of the art post-HF method. Couplings between excited potential energy surfaces result from diabaticization. We discuss wave packet evolution, population transfer and distribution. The delay time is compared to experimental results and we talk about the implications of our simulation.

MO 9: Posters 1: Dichroism, VUV and Xray, Clusters, and Cold Molecules

Time: Tuesday 17:00–19:00

Location: P OGs

MO 9.1 Tue 17:00 P OGs

Theoretical study of photoelectron circular dichroism in the multiphoton ionization of bicyclic ketones — ●ANNE DOROTHEE MÜLLER, ANTON N. ARTEMYEV, and PHILIPP V. DEMEKHIN — Institut für Physik, Universität Kassel, Heinrich-Plett-Str. 40, 34132 Kassel

Recently [1-3], it was demonstrated experimentally that absorption of several circularly polarized photons in the multiphoton ionization spectra of randomly oriented chiral molecules by femtosecond laser pulses may result in a considerable photoelectron circular dichroism (PECD) effect. So far, a reliable quantitative theoretical interpretation of these experimental results is missing. Here, we perform a systematical investigation of PECD in the resonance enhanced multiphoton ionization and above threshold ionization spectra of camphor and fenchone, by numerically solving the time-dependent Schrödinger equation for the single-active-electron wave-packet in a chiral molecular potential in the presence of intense circular polarized laser pulses [4]. Theoretical results obtained for randomly oriented and fixed-in space molecules are presented and compared with experiments [1].

[1] C. Lux *et al.*, *Angew. Chem. Int. Ed.* **51**, 5001 (2012); *ChemPhysChem* **16**, 115 (2015); *J. Phys. B* **49**, 02LT01 (2016).

[2] M. H. M. Janssen and I. Powis, *Phys. Chem. Chem. Phys.* **16**, 856 (2014).

[3] S. Beaulieu *et al.*, *New J. Phys.* **18**, 102002 (2016).

[4] A.N. Artemyev, A.D. Müller, D. Hochstuhl, and Ph.V. Demekhin, *J. Chem. Phys.* **142**, 244105 (2015).

MO 9.2 Tue 17:00 P OGs

Broadband Time-resolved Circular Dichroism Spectroscopy of Hemoglobin — ●HEIKO HILDENBRAND, ANDREAS STEINBACHER,

FEDERICO KOCH, MARCO SCHMID, and TOBIAS BRIXNER — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

Circular dichroism (CD) is a common technique for analyzing chiral samples by their difference in absorption of left and right circularly polarized light. However, chiral signals are small and the typically utilized long optical path lengths, high concentrations, and long integration times in steady-state measurements are not suitable for ultrafast spectroscopy. Hence, only few chirality-sensitive ultrafast time-resolved spectroscopic approaches in the liquid phase have been reported [1,2].

Here we present broadband time-resolved CD spectroscopy which is based on a setup capable of mirroring an arbitrary polarization state of an ultrashort laser pulse. Hence, by passing a circularly polarized broadband probe pulse through this setup we can switch between opposite handedness on a shot-to-shot basis to detect transient CD changes. To demonstrate the capabilities of this approach we investigate the early photochemistry of oxygenated hemoglobin and myoglobin by time-resolved circular dichroism and transient absorption spectroscopy in the visible spectral region, since the spectrometer is capable of acquiring both signals simultaneously.

[1] Meyer-Ilse *et al.*, *Laser Photon. Rev.* **7**, 495 (2013)

[2] Hiramatsu *et al.*, *J. Chem. Phys.* **143**, 121102 (2015)

MO 9.3 Tue 17:00 P OGs

Broadband Photoelectron Circular Dichroism — ●TOM RING, ALEXANDER KASTNER, PHILIPP HILLMANN, HENDRIKE BRAUN, ARNE SENFTLEBEN, and THOMAS BAUMERT — Universität Kassel, Institut für Physik und CINSaT, D-34132 Kassel

Photoelectron circular dichroism (PECD) describes the asymmetry in the photoelectron angular distribution (PAD) with regard to the light

propagation direction after ionization with circularly polarized light. First investigated by one photon synchrotron ionization,¹ we demonstrated that PECD on isotropically distributed chiral molecules is accessible via 2+1 resonance enhanced multi photon ionization (REMPI) using femtosecond laser pulses and established PECD as a highly sensitive and robust analytical tool.² A different excitation scheme is addressed within PECD studies of electrons from above threshold ionization (ATI).³

In this contribution we present an ultra-broadband approach to PECD using white light generated by an argon filled hollow-core fiber. This way the excitation scheme changes due to the combination of different wavelengths with regard to the temporal structure of the pulses and a wide range of excess energies in the PADs can be accessed simultaneously.

[1] L. Nahon et al.: *J. El. Spectr. Rel. Phen.*, **204**, 322 (2015)

[2] C. Lux et al.: *Chem. Phys. Chem* **16**, 115 (2015)

[3] C. Lux et al.: *J. Phys. B* **49**, (2016)

MO 9.4 Tue 17:00 P OGS

Towards continuous-wave cavity-enhanced polarimetry for highly sensitive chirality measurements — ●OLEG TRETIK¹, LYKOURGOS BOUGAS¹, DIONYSIS ANTYPAS², and DMITRY BUDKER^{1,2} — ¹Johannes Gutenberg Universität Mainz, 55128 Mainz, Germany — ²Helmholtz Institut Mainz, 55128 Mainz, Germany

We present our work towards the construction of a cavity-enhanced polarimeter for highly sensitive, continuous-wave, measurements of chirality in the gas, liquid, and solid phase. The developed polarimeter employs an optical cavity that allows for the enhancement of the chiral (optical-rotation) signals by the number of cavity passes, and, for the introduction of crucial signal reversals that enable absolute chirality measurements with high sensitivity. The presented technique has applications in different science fields ranging from fundamental physics, to atmospheric chemistry and medical research. We present our newly constructed chiral-polarimeter here in Mainz, and discuss its current sensitivity and our efforts towards shot-noise limited optical rotation measurements.

MO 9.5 Tue 17:00 P OGS

Transient absorption and VCD spectroscopy of two azobenzene derivatives with chiral sidegroups — ●KEVIN ARTMANN¹, KAROLINE BUENNEMANN², JOHANNES KNORR¹, CHRISTIAN MERTEN², and PATRICK NUERNBERGER¹ — ¹Physikalische Chemie II, Ruhr-Universität Bochum, 44780 Bochum — ²Organische Chemie II, Ruhr-Universität Bochum, 44780 Bochum

Azobenzenes are a widely-studied class of photochromic molecular switches with versatile applicability. Their photoswitching is based on a *trans/cis* isomerization, with the exact isomerization mechanism still under debate and subject of many recent investigations [1]. We examine two azobenzene derivatives with chiral sidegroups: the one substituted in para position, whose *cis* isomer is observable for >48 h after photoswitching, shows ultrafast dynamics similar to unsubstituted azobenzene [2]. Global analysis yields three time constants for accurately describing the experimental data. The second azobenzene derivative, with two substituents in *ortho* position, behaves differently: the *cis* isomer is absent in stationary absorption spectra, yet transient absorption discloses that it is formed. Hence, a fast thermal back-isomerization occurs, caused by electronic and/or steric effects of the sidegroups. The experiments are complemented with IR and vibrational circular dichroism (VCD) studies: switching is observed in vibrational spectra for the *para* compound, whereas the fast back-reaction prevents the observation of VCD changes for the *ortho* compound.

*[1] H.M.D. Bandara, S.C. Burdette, *Chem. Soc. Rev.* **41**, 1809 (2012).

*[2] I.K. Lednev *et al.*, *Chem. Phys. Lett.* **290**, 68 (1998).

MO 9.6 Tue 17:00 P OGS

Angle-resolved spectroscopy of electron emission by chiral molecules — ●DANIEL ROMAN PAUL, JAN DREISMANN, and STEFAN SCHIPPERS — I. Physikalisches Institut, Justus-Liebig-Universität Gießen

In elementary particle physics chirality is of great importance, in particular for the weak interaction. According to the Vester-Ulbricht-hypothesis a symmetry breaking by the weak interaction might be a reason for homochirality of molecules of life. While chemical properties of chiral molecules are already well observed, the physical basis is still a topic of current research. In this context collision experiments can give insight into the electronic structure and electron dynamics of

chiral molecules.

We use an ESA22 [1,2] electron spectrometer for angle- and energy-resolved electron spectroscopy. Electrons produced by the collision of spin-polarized electrons as well as circular polarized photons on a gas target are separated by energy via a combination of electrostatic fields and detected by 22 channel electron detectors.

We here report on electron collisions on methyl lactate ($C_4H_8O_3$). The resulting Auger spectra are compared with Auger spectra for oxygen and carbon dioxide, measured under similar conditions.

[1] Ricz et al., *Phys. Rev. A* **65**, 042707 (2002)

[2] Ábrók et al. *Nucl. Instr. Meth. Phys. Res. B* **369** (2016) 24-28

MO 9.7 Tue 17:00 P OGS

Electron-nuclear Coupling through Autoionizing States after Strong-field Excitation of H₂ Molecules — ●YONGHAO MI, NICOLAS CAMUS, LUTZ FECHNER, MARTIN LAUX, ROBERT MOSHAMMER, and THOMAS PFEIFER — Max-Planck-Institute for Nuclear Physics, Saupfercheckweg 1, 69117 Heidelberg

Channel-selective electron emission from strong-field photo-ionization of H₂ molecules is experimentally investigated by using ultrashort laser pulses and a Reaction Microscope. The electron momenta and energy spectra in coincidence with bound and dissociative ionization channels are compared. Surprisingly, we observed an enhancement of the photoelectron yield in the low-energy region for the bound ionization channel. By further investigation of asymmetrical electron emission using two-color laser pulses, this enhancement is understood as the population of the autoionizing states of H₂ molecules in which vibrational energy is transferred to electronic energy.

MO 9.8 Tue 17:00 P OGS

Imaging of the He₂ wave function using a free electron laser — ●STEFAN ZELLER¹, MAKSYM KUNITSKI¹, JÖRG VOIGTSBERGER¹, ANTON KALININ¹, ALEXANDER SCHOTTELIUS¹, CARL SCHOBER¹, MARKUS WAITZ¹, HENDRIK SANN¹, ALEXANDER HARTUNG¹, TOBIAS BAUER¹, MARTIN PITZER¹, FLORIAN TRINTER¹, CHRISTOPH GOHL¹, CHRISTIAN JANKE¹, MARTIN RICHTER¹, GREGOR KASTIRKE¹, MIRIAM WELLER¹, ACHIM CZASCH¹, MARKUS BRAUNE², ROBERT E. GRISENTI^{1,3}, LOTHAR PH. H. SCHMIDT¹, MARKUS S. SCHÖFFLER¹, JOSHUA B. WILLIAMS⁴, TILL JAHNKE¹, and REINHARD DÖRNER¹ — ¹Institut fuer Kernphysik, Goethe-Universität Frankfurt, 60438 Frankfurt, Germany — ²Deutsches Elektronen-Synchrotron, 22607 Hamburg, Germany — ³GSI Helmholtz Centre for Heavy Ion Research, 64291 Darmstadt, Germany — ⁴Department of Physics, University of Nevada, Reno, NV 89557, USA

We report on Coulomb explosion imaging of the wavefunction of the quantum halo system He₂. Each atom of this system is ionized by tunnel ionization in a femto second laser pulse and in a second experiment by single photon ionization employing a free electron laser. We visualize the exponential decay of the probability density of the tunneling particle over distance for over two orders of magnitude up to an internuclear distance of 250 Å. By fitting the slope of the density in the tunneling regime we obtain a binding energy of 151.9 ± 13.3 neV, which is in agreement with most recent calculations [Przybytek et al., PRL **104**, 183003, 2010].

MO 9.9 Tue 17:00 P OGS

Ultrafast photodissociation of small molecules studied by interferometric VUV-VUV pump-probe experiments — OLIVER SCHEPP¹, ARNE BAUMANN¹, MAREK WIELAND^{1,2,3}, and ●MARKUS DRESCHER^{1,2,3} — ¹Institut für Experimentalphysik, Universität Hamburg, Luruper Chaussee 149, 22761 Hamburg — ²The Hamburg Centre for Ultrafast Imaging (CUI), Luruper Chaussee 149, 22761 Hamburg — ³Centre for Free-Electron-Laser Science, Universität Hamburg, Luruper Chaussee 149, 22761 Hamburg

Ultrafast photoreaction dynamics of small molecules are studied in the time domain, using a single-color VUV-pump/ VUV-probe scheme [1]. 17-fs VUV-pulses, centered at 161 nm with pulse energies up to 1.1 μJ created with high harmonic generation are split by two moveable interdigitated double comb mirrors into two collinearly propagating replicas with a variable delay [2,3]. This Michelson-type all-reflective interferometric autocorrelation scheme is used for recording the time-dependent pump-probe signal with simultaneous non-resonant two-photon ionization of krypton as a precise timing-reference. The photoreaction dynamics are probed via one and two VUV photon absorption, enabling different observables for the pump-probe signal which expands intrinsic limitations in observation of the molecular wavepacket. Additional spectral information obtained by the interferometric resolution

give access to the involved harmonic orders and the order of nonlinearity.

- [1] Schepp, O. et. al., Phys Rev. A 94, 033411 (2016)
- [2] Rompotis, D. et. al., Opt. Lett. 50 1675 (2015)
- [3] Gebert, T., et al., New J. Phys. 16 0170347 (2014)

MO 9.10 Tue 17:00 P OGS

Experimental set-up for dispersed photon emission spectroscopy of liquid microjets — ●CHRISTIAN OZGA¹, ANDREAS HANS¹, ROBERT SEIDEL², PHILIPP SCHMIDT¹, XAVER HOLZAPFEL¹, MARVIN POHL², BERND WINTER², ARNO EHRESMANN¹, and ANDRÉ KNIE¹ — ¹Institut für Physik und Center for Interdisciplinary Nanostructure Science and Technology (CINSA-T), Universität Kassel, Heinrich-Plett-Straße 40, 34132 Kassel, Germany — ²Helmholtz-Zentrum für Materialien und Energie, Albert-Einstein-Straße 15, 12489 Berlin, Germany

With the development of liquid microjets the interest in the investigation of the molecular structure of volatile liquids after X-ray irradiation increased progressively. This structure was probed by different measurement techniques ranging from the detection of charged particles, Raman spectroscopy to X-ray emission spectroscopy and revealed e.g. interatomic coulombic decay processes in liquid water as well as different types of hydrogen bonds in bulk liquid water. However, the low energy photon emission regime, i.e. the wavelength region from 40 nm to 650 nm, remains hitherto unexplored. This spectral range acts as a complementary tool for the other techniques allowing a deeper understanding of the still not fully understood molecular structure of liquids, solvated (bio-)molecules and the interaction of solvents and solutes. Here we present an experimental set-up for the detection of dispersed photons with emission wavelengths from 40 nm to 650 nm. It can be easily adapted for the additional measurement of photoelectrons allowing a direct comparison of photon and electron emission.

MO 9.11 Tue 17:00 P OGS

From Rare Gas to Hydrogen-bonded clusters: Size distributions of supersonic beams from a pulsed valve using the titration technique — ●MATTHIAS BOHLEN, AARON LAForge, RUPERT MICHIELS, NICOLAS RENDLER, MYKOLA SHCHERBININ, and FRANK STIENKEMEIER — Institute of Physics, University of Freiburg, Hermann-Herder-Str.3, D-79104 Freiburg i.B.

Pulsed valves, in general, offer many advantages over continuous beam sources such as higher beam densities and reduced gas load. Recently, we developed a pulsed valve in collaboration with UBC, Vancouver, which produces supersonic gas pulses down to 20 μ s duration at repetition rates up to several hundred Hz. Overall, the valve is versatile in the type of clusters which can be produced ranging from rare gas clusters to hydrogen bonded clusters. Additionally, cryogenic cooling of the valve can be utilized to produce helium nanodroplets. To estimate the cluster size distribution, we use the so-called titration technique [1], which has accurately determined cluster sizes of continuous supersonic beams. Here, we report on a systematic study of cluster size distributions by varying expansion parameters. We apply this technique to argon, ammonia, and water clusters.

[1] L. F. Gomez, E. Loginov, R. Sliter, A. F. Vilesov; J. Chem. Phys. 135, 154201 (2011)

MO 9.12 Tue 17:00 P OGS

Small metal clusters on porphyrin templates — ●FREDERIC USSLING¹, TOBIAS BISCHOFF¹, ANDRE KNECHT¹, ANDREA MERLI¹, MERLE I. S. RÖHR², POLINA G. LISINETSAYA², JENS PETERSEN², ROLAND MITRIĆ², THOMAS MÖLLER¹, and TORBJÖRN RANDER¹ — ¹Institut für Optik und Atomare Physik, Technische Universität Berlin — ²Institut für Physikalische und Theoretische Chemie, Universität Würzburg

The size- and structure-dependent optical properties of metal clusters have been studied for many years. In the smallest size regime, every single atom is known to have a high impact on both the cluster geometry and optical properties [1]. Several years ago, first studies on the collective optical characteristics and interactions between multiple clusters, and the influence of their orientation were carried out [2]. Recently, it has been predicted that porphyrin templates may be used to produce well defined arrangements of small metal clusters [3]. However, so far, no experimental verification exists. We investigated the possibility to combine cationic Cu₃ clusters with single porphyrins in a collision cell. This represents a first step towards investigating metal clusters on porphyrin templates in the gas phase.

- [1] K. L. Kelly et. al., J. Phys. Chem. B 107, 668 (2003)
- [2] P. G. Lisinetskaya et. al., Phys. Rev. B 89, 035433 (2014)
- [3] M. Röhr et. al., J. Phys. Chem. A 120, 4465 (2016)

MO 9.13 Tue 17:00 P OGS

Untangling the far-infrared/fingerprint region of the absorption spectrum of small water clusters using helium droplet spectroscopy — ●RAFFAEL SCHWAN¹, DEVENDRA MANI¹, NITISH PAL¹, GERHARD SCHWAAB¹, BRITTA REDLICH², LEX VAN DER MEER², and MARTINA HAVENITH¹ — ¹Physikalische Chemie II, Ruhr-Universität Bochum — ²Institute for Molecules and Materials (IMM), Radboud University Nijmegen

The molecular understanding of water-water interactions has been subject of numerous experimental and theoretical studies. The intramolecular modes of water clusters (H₂O)_n with $n \leq 6$ are well investigated in the mid-infrared and in the fingerprint region while there are only few experimental studies treating the far-infrared region. This region is mainly dominated by intermolecular motions. The most prominent one is the librational band ranging from 300 to 1000 cm⁻¹ in H₂O.

Recently, we have combined our helium droplet spectrometer with the free electron laser at the FELIX facility, Radboud University Nijmegen. Helium droplets provide a soft matrix suited well for spectroscopic investigations. They enable the step-wise formation and stabilization of weakly bound aggregates at low temperatures of 0.37 K. In combination with mass selective and pressure dependent measurements, helium droplet spectroscopy becomes a powerful tool for assigning spectral signals to distinct aggregates. Here, we show the absorption spectra of small water clusters in the frequency range of the FELIX radiation source and their assignment based on pressure dependent measurements and accompanying calculations.

MO 9.14 Tue 17:00 P OGS

The role of dispersion interactions on the microsolvation of aromatic ethers — ●FABIAN DIETRICH, DOMINIC BERNHARD, MARKUS BURKHART, MAXIMILIAN LUCZAK, and MARKUS GERHARDS — TU Kaiserslautern & Research Center Optimas, Erwin-Schrödinger-Str. 52, 67663 Kaiserslautern

Aromatic ethers offer different hydrogen bond acceptor sites for the interaction with polar solvent molecules like alcohols or water. Depending on the aromatic group and the second moiety the preference switches from an OH-O hydrogen bonded structure to an OH- π structure which is a consequence of dispersion interactions. We investigated the diphenyl ether (DPE) aggregated with one and two water molecules as well as phenyl vinyl ether (PVE) with methanol. This work is a comparison of different quantum chemical methods (DFT-D3, SCS-CC2) with combined IR/UV spectroscopy in the electronic ground state and first excited state inside the priority program SPP 1807.

For DPE complexes with one water the investigation of the OH-stretching vibration leads to the conclusion that the OH- π motif (compared to the OH-O motif) is dominant, as also predicted by theory. The cluster with two water contains both motifs as well as a hydrogen bond between both water molecules. For the PVE/methanol cluster three structures are predicted: one with an OH- π bond to the phenyl group, a further one with an OH-O arrangement and one isomer with an OH- π bond to the ethenyl moiety. All three structures are observed spectroscopically. In the excited state of the PVE/methanol complex a structural rearrangement is expected.

MO 9.15 Tue 17:00 P OGS

Dissociative electron attachment in small clusters of ammonia and formic acid — ●MARVIN WEYLAND¹, ALEXANDER DORN¹, XUEGUANG REN¹, HANS RABUS², and WOON YONG BAEK² — ¹Max Planck Institute for Nuclear Physics, Saupfercheckweg 1, 69117 Heidelberg, Germany — ²Physikalisch-Technische Bundesanstalt, Bundesallee 100, 38116 Braunschweig, Germany

Dissociative electron attachment (DEA) has been identified as a possible process for radiation damage. In short, DEA is a resonant two-step process in which first a low-energetic electron is captured by a molecule. The created negative ion can subsequently dissociate while the captured electron stays attached to one of the fragments. Most experiments however have been carried out on isolated gas phase molecules. We show the influence of clustering on the dissociation resonance energies and the fragmentation channels, thereby recreating effects which occur in the liquid phase.

Our experiments are carried out in a COLTRIMS type negative ion spectrometer and the electron beam is created using a photo-emission electron source, yielding a good combination of energy resolution and

current. In ammonia cluster fragments of up to 17 molecules we observe an increase of the dissociation energy of up to 0.3 eV compared to the isolated molecule. In formic acid dimers and trimers on the other hand the impact energy for the highest dissociation yield is lowered with increasing fragment size, with impact energy for production of the fragments differing by up to 1 eV. We propose different effects which influence the dissociation path to explain our observations.

MO 9.16 Tue 17:00 P OGs

BerlinTrap: A novel cryogenic 22-pole tandem mass spectrometer — ●PABLO NIETO, ALAN GÜNTHER, DAVID MÜLLER, ALEX SHELDRICK, and OTTO DOPFER — Institut für Optik und Atomare Physik, Technische Universität Berlin, Hardenbergstr. 36, D-10623 Berlin, Germany

We present the design and first applications of a new tandem mass spectrometer (BerlinTrap) combining an electrospray ion source, a quadrupole mass spectrometer, a cryogenic 22-pole ion trap (4-300 K), and an orthogonal reflectron time-of-flight mass spectrometer [1]. The trapped ions are cooled by helium buffer gas cooling. The formation and solvation shell structure of weakly-bound $\text{He}_n\text{H}_3\text{O}^+$ complexes and the electronic photodissociation spectrum of the protonated amino acid tyrosine are used to calibrate the setup for cooling, tagging, and spectroscopic capabilities. A vibrational temperature below 20 K is inferred for protonated tyrosine. The electronic spectrum of isolated protonated lumichrome, the smallest protonated flavin, is recorded in the visible range and assigned to the most stable N5 isomer by comparison with quantum chemical calculations. These results demonstrate the suitability of the BerlinTrap apparatus for spectroscopy and reactivity studies of small and large (bio-)molecular ions and their clusters.

[1] A. Günther, P. Nieto, D. Müller, A. Sheldrick, D. Gerlich, and O. Dopfer, *J. Mol. Spectrosc.*, in press, DOI:10.1016/j.jms.2016.08.017

MO 9.17 Tue 17:00 P OGs

Towards high resolution spectroscopy of biomolecular ions in a cryogenic multipole ion trap — ●FELIX DUENSING, STEFFEN SPIELER, LENA REMMERS, MORITZ FISCHER, KATHARINA GEISTLINGER, and ROLAND WESTER — Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck, Österreich

High resolution spectroscopy is a versatile method to study molecular structures [1]. At room temperature many close lying rovibrational states are populated, which can make the interpretation difficult. Several biomolecular ionic complexes have already been investigated in combination with buffer gas cooling [2,3]. Our approach combines spectroscopy of charged biomolecular systems and weakly bound clusters with high resolution far-infrared techniques in a radio frequency ion trap setup similar to Ref. [4]. With quadrupole guides and filters we are able to load ions mass selectively in a 16-pole wiretrap cooled to below 4 K. Buffer gas is used to cool the rovibrational states and a reflectron type time of flight mass spectrometer detects the ions. Action spectroscopy on the trapped and cooled ions can be performed perpendicular to the trap axis by means of narrow band infrared lasers and THz radiation. The latest status on vibrational spectroscopy of amino acids and water clusters will be presented.

[1] Spaun, B., et al., *Nature*, 533, 2016, 517.

[2] Boyarkin, O. V., et al., *J. Am. Chem. Soc.*, 128, 2006, 2816.

[3] Kamrath, M. Z., et al., *J. Am. Chem. Soc.*, 133, 2011, 6440.

[4] Günther, A., et al., *J. Mol. Spec.*, 2016.

MO 9.18 Tue 17:00 P OGs

Spectroscopy on cold molecules using a chirped pulse microwave spectrometer — ●PASCAL STAHL¹, THOMAS GIESEN¹,

GUIDO FUCHS¹, and JOHANNA CHANTZOS² — ¹Institut für Physik, Universität Kassel, 34132 Kassel, Germany — ²Max-Planck-Institut für extraterrestrische Physik, 85741 Garching bei München, Germany

We present a novel technique to investigate molecules in the gas phase in the K- and W-band. The new experimental setup comprises an absorption spectrometer in combination with a supersonic jet.

The purpose of the setup is to detect short-living and small molecules at low temperatures. For this a twin-channel arbitrary waveform generator (AWG) with 400 MS/s sample rate and 145 MHz analog bandwidth emits a (linear) chirp both in phase and as quadrature signal (I/Q-signal). Using a single sideband upconverter this signal is mixed with a carrier signal in the GHz regime that has been produced by a synthesizer. The resulting (mixed) signal is amplified and sent into a coaxial waveguide adapter and horn antenna to be broadcasted into a vacuum chamber. There the radiation interacts with molecules and in case of an absorption the reduced signal is detected via a horn-antenna-detector device (zero bias shottky diode). The signal is then digitized and sent to a computer.

We have measured ammonia, nitrous oxide as well as acetonitrile. In combination with a discharge nozzle the spectrometer allows to produce and detect a variety of volatile molecules that are of astrophysical and astrochemical interest.

MO 9.19 Tue 17:00 P OGs

Sympathetic cooling of anions in a hybrid atom-ion trap

— ●TOBIAS HELDT¹, HENRY LOPEZ¹, BASTIAN HÖLTKEMEIER¹, JONAS TAUCH¹, ERIC ENDRES², ROLAND WESTER², and MATTHIAS WEIDEMÜLLER¹ — ¹Physikalisches Institut Heidelberg, INF 226, 69120 Heidelberg — ²Institut für Ionenphysik und Angewandte Physik, Technikerstraße 25/3, 6020 Innsbruck

In our experimental setup OH^- ions are confined in an octupole radio-frequency trap, where they can be superimposed by laser-cooled rubidium atoms in a dark spontaneous-force optical trap. By localising the atom cloud to the centre of the trap sympathetic cooling of the anions can be achieved even for atom-to-ion mass ratios bigger than unity. The differences between our two experimental approaches of probing the ion distribution, namely photodetachment tomography and time-of-flight analysis, will be discussed in particular.

MO 9.20 Tue 17:00 P OGs

Controlling Cold Atom-ion Collisions Using Rydberg States

— ●LIMEI WANG, MARKUS DEISS, and JOHANNES HECKER DEN-SCHLAG — Inst. f. Quantenmaterie, Universität Ulm

We propose a scheme where the cold collision between an ultracold Rb atom and a trapped single Ba^+ ion will be controlled by a 'blue shielding laser'. During the collision, the laser excites the Rb atom to a repulsive electronically excited molecular state formed by the Rydberg atom and ion once the atom approaches to a certain internuclear distance. In this way the ion is effectively surrounded by a hard potential wall that the atom cannot cross. Once the atom leaves the interaction area, it is de-excited back in an adiabatic way to its original level. By controlling the laser power and the laser frequency, as well as by addressing different Rydberg states, the properties of this 'shielding' can be widely tuned. Long-range shielding effects are expected to be realized with higher n Rydberg states.

An important application of the collision control is to suppress unwanted chemical reactions between atoms and ion, such as charge exchange or three-body recombination. The suppression of inelastic collisions is an essential tool required for the young developing field of cold atom-ion hybrid systems where in general only elastic collisions are desired.

MO 10: Highly Excited Molecules and Clusters

Time: Wednesday 14:30–16:30

Location: N 6

Invited Talk

MO 10.1 Wed 14:30 N 6

Molecular movies of migrating protons on different paths

— ●HEIDE IBRAHIM¹, VINCENT WANIE¹, SAMUEL BEAULIEU¹, BENJI WALES², BRUNO SCHMIDT¹, XIAO-MIN TONG³, JOE SANDERSON², MICHAEL SCHUURMAN⁴, and FRANÇOIS LÉGARÉ¹ — ¹INRS-EMT, 1650 Blvd. Lionel-Boulet, J3X 1S2, Varennes (Qc) Canada — ²University of Waterloo, 200 University Av. West, Waterloo, Ontario, Canada N2L 3G1 — ³University of Tsukuba, Ibaraki, 305-8577 Japan

— ⁴NRC, 100 Sussex Dr, Ottawa, Ontario, Canada K1A 0R6

How do atoms move within a molecule? What are the paths they take? Coulomb Explosion Imaging combined with a multi-color pump probe scheme allows us to address these questions with a table top setup. Since the momentum information of molecular fragments is preserved at the moment of explosion we can deduce their momentary position, representing the structure of the molecule. We have studied isomerization and dissociation events through the movement of

protons, deuterons and electrons, taking advantage of the rich statistics this technique provides. In the case of proton migration in the acetylene cation were able to identify an isotope dependent to- and fro isomerization behavior [1]. Presently, we are expanding our studies on more complex processes. Aside from passively studying dynamics, we have also actively controlled the electron localization in small molecules using two-color mid-infrared asymmetric laser fields [2].

[1] H.Ibrahim et al., Nature commun. 5:4422 (2014)

[2] V. Wanie et al., J. Phys. B: At. Mol. Opt. Phys. 49 025601 (2016)

MO 10.2 Wed 15:00 N 6

Ultrafast Isomerization in Acetylene Dication: To Be or Not To Be — ZHENG LI^{1,2}, LUDGER INHESTER¹, CHELSEA LIEKHUS-SCHMALTZ², ORIOL VENDRELL³, and TODD MARTINEZ² — ¹CFEL, DESY, Notkestr. 85, D-22607 Hamburg, Germany — ²SLAC National Accelerator Laboratory, CA 94025 Menlo Park, USA — ³Department of Physics and Astronomy, Aarhus University, 8000 Aarhus, Denmark

The mechanism for ultrafast isomerization of acetylene [HCCH]²⁺ to vinylidene [H₂CC]²⁺ dication is nebulous. Theoretical studies show a large potential barrier (>2eV) for isomerization pathways, implying that the corresponding isomerization should take picoseconds or even longer. However a recent experiment at a femtosecond X-ray free electron laser (XFEL) suggests that large amplitude hydrogen migration proceeds on a sub-100 femtosecond time scale [1]. We present a complete theoretical study of dynamics of acetylene dication produced by Auger decay after X-ray photoionization of carbon K-shell. We find that isomerization does not occur on the sub-100 fs timescale and is not required to explain the time-resolved Coulomb imaging experiment. This study resolves the seeming contradiction between experiment and theory concerning the isomerization time scale in acetylene dication. This work calls for careful interpretation of structural information from the widely applied Coulomb momentum imaging method but also points out its strengths in mapping out momentum dispersion dynamics even when structural variation is minor [2].

[1] Ch. Liekhus-Schmaltz et al., Nature Commun. 6, 8199 (2015).

[2] Z. Li et al., arXiv:1605.05707, submitted.

MO 10.3 Wed 15:15 N 6

Single-Shot Pump-Probe Studies in a Two Color (V)UV Field — ARNE BAUMANN^{1,2}, OLIVER SCHEPP¹, DIMITRIOS ROMPOTIS³, ARMIN AZIMA¹, MAREK WIELAND^{1,2,4}, and MARKUS DRESCHER^{1,2,4} — ¹Institut für Experimentalphysik, Universität Hamburg, Hamburg, Deutschland — ²Hamburg Centre for Ultrafast Imaging - CUI, Hamburg, Deutschland — ³Deutsches Elektronensynchrotron - DESY, Hamburg, Germany — ⁴Center for Free-Electron-Laser Science - CFEL, Hamburg, Germany

To gain a complete picture of few-femtosecond (V)UV-induced reactions delay-dependent ionization of parent and fragment ions by weak probe photons is an excellent tool. The presented single-shot pump-probe scheme is based on wave-front splitting of intense harmonic radiation of a Ti:Sa laser system. Individual pulses are focused anti-parallelly into a gas target and ions created are imaged onto a position-sensitive detector, thus mapping the temporal delay between both pulses onto a spatial coordinate. By using different dielectric mirrors and/or filters for each pulse, a two-color cross-correlation and pump-probe experiment is realized, benefiting from single-shot acquisition capabilities.

The multiphoton UV-dissociation dynamics of formaldehyde have been studied with an intense 5th harmonic (161.8 nm) probe after irradiation at 269.7 nm. The 7.7 eV probe enables studies of the delay-dependent dissociative ion-yield for various fragments of this dissociation reaction in a perturbative approach.

MO 10.4 Wed 15:30 N 6

Time-Resolved XUV-induced Electron Solvation Dynamics in Ammonia and Water Clusters — RUPERT MICHIELS¹, AARON LAFORGE¹, MATTHIAS BOHLEN¹, CARLO CALLEGARI², ANDREW CLARK³, MARCEL DRABBELS³, KEVIN C. PRINCE², STEFANO STRANGES⁴, MARCELLO CORENO⁵, PAOLA FINETTI², OKSANA PLEKAN², JUN MA⁶, VERONICA OLIVER³, HANS-JAKOB WÖRNER⁶, and FRANK STIENKEMEIER¹ — ¹Universität Freiburg, Germany — ²Elettra-Sincrotrone Trieste, Italy — ³Ecole Polytechnique Fédérale de Lausanne, Switzerland — ⁴University Sapienza, Italy — ⁵CNR - Istituto di Struttura della Materia, Italy — ⁶ETH Zürich, Switzerland

The solvation of electrons in aqueous solutions plays an important role

in biological and chemical systems. Nonetheless, a fundamental understanding of its properties (e.g. solvation time, binding energies, solvation shells, and binding motifs) has yet to be fully attained. Here, we report new results for ammonia and water clusters investigating XUV ionization followed by electron recapture. The binding energies of the solvated electron were measured in a pump-probe scheme as a function of cluster size in which we found solvation times in the femtosecond to picosecond range.

MO 10.5 Wed 15:45 N 6

Multi-state Photoelectron Circular Dichroism in Femtosecond Multiphoton Ionization — ALEXANDER KASTNER, STEFANIE ZÜLLIGHOVEN, TOM RING, CRISTIAN SARPE, ARNE SENFTLEBEN, and THOMAS BAUMERT — Universität Kassel, Institut für Physik und CIN-SaT, D-34132 Kassel, Germany

The asymmetry of photoelectron angular distributions (PADs) from randomly oriented enantiomers of chiral molecules in the ionization with circularly polarized light arises in forward/backward direction with respect to the light propagation. This effect was termed Photoelectron Circular Dichroism (PECD) and so far investigated using synchrotron radiation [1, 2]. We observed highly structured asymmetries in the range of +/- 10 % on bicyclic Ketones [3, 4].

Due to the multi photon ionization (MPI), high order Legendre polynomials appear in the measured PADs. In the case of Resonance Enhanced MPI (REMPI) using different intermediate states, the contributions in the photoelectron spectrum depend on wavelength. By changing wavelength and intermediate states, we are able to investigate PECD depending on photoelectron kinetic energy.

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

[2] L. Nahon et al., J. El. Spectr. 204, 322-334, (2015)

[3] C. Lux et al., Chem. Phys. Chem. 16, 115-137, (2015)

[4] A. Kastner et al., Chem. Phys. Chem. 17, 1119-1122, (2016)

MO 10.6 Wed 16:00 N 6

Comparing UV and strong-field induced dynamics in selenophene probed by femtosecond XUV transient absorption spectroscopy — FLORIAN LACKNER^{1,2,3}, ADAM S. CHATTERLEY^{1,2}, C. D. PEMMARAJU^{1,4}, KRISTINA D. CLOSSER⁴, DAVID PRENDERGAST⁴, DANIEL M. NEUMARK^{1,2}, STEPHEN R. LEONE^{1,2,5}, and OLIVER GESSNER¹ — ¹Chemical Sciences Division, Lawrence Berkeley National Lab — ²Department of Chemistry, UC Berkeley — ³Institute of Experimental Physics, TU Graz — ⁴The Molecular Foundry, Lawrence Berkeley National Lab — ⁵Department of Physics, UC Berkeley

UV and strong-field induced dynamics in selenophene (C₄H₄Se) molecules are studied by femtosecond transient inner-shell absorption spectroscopy at the Se 3d edge. Spectra obtained upon strong-field ionization are dominated by emerging bare Se ions produced in a sequential two-step mechanism, whereby the initial ring-opening and the subsequent fragmentation are associated with two characteristic time-scales of $\tau_1 \approx \tau_2 \approx 80$ fs. In contrast, excitation with a moderately intense UV (266 nm) pump pulse gives predominantly rise to the formation of bare Se atoms and a smaller contribution of Se ions. The ionic contribution increases with UV intensity. In both cases, spectral signatures of stable molecular products are found as well, which are assigned based on TDDFT calculations. Independent of the excitation/ionization scheme, the braking of both C-Se bonds is the dominant relaxation channel in selenophene, which can be traced in real-time by XUV transient absorption spectroscopy.

MO 10.7 Wed 16:15 N 6

Time-resolved Photoionisation of the S2 ($\pi\pi^*$) State of Xanthone — MARCO FLOCK, HANS-CHRISTIAN SCHMITT, and INGO FISCHER — Julius-Maximilians University of Würzburg, Institute of Physical and Theoretical Chemistry, Am Hubland, 97074 Würzburg, Germany

Previous studies on Fluorenone, NDCA and Naphthalimide showed, that relaxation processes in such aromatic heterocycles are determined by a competition between internal conversion (IC) and intersystem crossing (ISC). Which relaxation pathway is preferred depends strongly on the vibrational levels of the excited states. As a further representative of the group of aromatic heterocycles, we investigated the excited state dynamics of the S2 ($\pi\pi^*$) state of Xanthone. In a jet-cooled photoionization experiment, we resolved the vibronic properties of this state and found a defined structure with well-resolved vibronic bands. In time-resolved experiments, we found a depopulation of the S2 state

with two time constants $\tau(1) < 1$ ps and $\tau(2) = 24$ ps followed by a constant signal offset, which occurs from the population of the long-lived T1 ($n\pi^*$) state. Thus, two relaxation pathways can be mentioned. In a first model, IC to the S1 ($n\pi^*$) state followed by an ISC process to the T1 ($n\pi^*$) state could take place. In another model, the first

time constant belongs to a fast ISC process to the T2 ($\pi\pi^*$) state, whereas the slower time constant represents a following IC process to the long-lived T1 ($n\pi^*$) state. In both models, El-Sayed forbidden ISC processes may take place.

MO 11: Molecular Nanostructures and Solids

Time: Wednesday 14:30–16:30

Location: N 25

MO 11.1 Wed 14:30 N 25

Superradiance from two dimensional brick-wall aggregates of dye molecules: the role of size and shape for the temperature dependence — ●ALEXANDER EISFELD¹, CHRISTIAN MARQUARDT², and MORITZ SOKOŁOWSKI² — ¹MPI-PKS — ²Uni Bonn

Aggregates of interacting molecules can exhibit electronically excited states which are coherently delocalized over many molecules. This can lead to a strong enhancement of the fluorescence decay rate which is referred to as superradiance (SR). To date, the temperature dependence of SR is described by a $1/T$ law. Using an epitaxial dye layer and a Frenkel-exciton based model we provide both experimental and theoretical evidence that significant deviations from the $1/T$ behaviour can occur for brickwall-type aggregates of finite size leading even to a maximum of the SR at finite temperature. This is due to the presence of low energy excitations of weak or zero transition strength. These findings are relevant for designing light-emitting molecular materials.

MO 11.2 Wed 14:45 N 25

Thermal Fluctuations of Frenkel Exciton Hamiltonian — ●PER-ARNO PLÖTZ¹, JÖRG MEGOW², THOMAS NIEHAUS³, and OLIVER KÜHN¹ — ¹Institut für Physik, Universität Rostock, Germany — ²Institut für Chemie, Universität Potsdam, Germany — ³Institute Lumière Matière, Université Lyon 1, France

Effects of thermal fluctuations on the electronic excitation energies and intermonomeric Coulomb couplings are investigated via density functional theory based tight binding in the linear response formulation (TD-DFTB) and ground state classical molecular dynamics. As a result, a parametrised Frenkel exciton Hamiltonian is obtained, with the effect of exciton-vibrational coupling being described by spectral densities. Employing dynamically defined normal modes, these spectral densities are analysed in great detail, thus providing insight into the effect of specific intramolecular motions on excitation energies and Coulomb couplings. First application is a PTCDI crystal where results based on force field trajectories are compared to DFTB driven trajectories. Further application is applied in combination with a QM/MM approach on a BChl_a dimer in solution.

MO 11.3 Wed 15:00 N 25

Coherent Two-Dimensional Spectroscopy of Exciton-Exciton Interactions — ●JAKUB DOSTÁL¹, FEDERICO KOCH¹, STEFANIE HERBST², PAWARET LEOWANAWAT², FRANK WÜRTNER², 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

Many important light-induced processes in molecular systems rely on multi-photon excitation of the sample. The studying of such processes requires reliable discrimination between the multi- and single-exciton signals, which might become a challenging task for many common methods of time-resolved spectroscopy.

Here we show that the fifth-order three-pulse optical signal characterized by the $-2k_1 + 2k_2 + k_3$ phase-matching relation is specific to bi-exciton processes, i.e., it emerges only if the presence of one exciton in the sample influences the behavior of another one. Further we show how this signal can be used for construction of two-dimensional spectrum of exciton-exciton interactions (EEI 2D) and derive some of its properties. The entire concept is experimentally demonstrated on the exciton annihilation process present in perylene bisimide J-aggregates. We observe the rise of the EEI signal as pairs of initially independent excitons located along one of the aggregate strains are brought together by the random diffusive motion and annihilate.

The proposed EEI 2D method can provide detailed understanding of versatile bi-exciton processes in molecular systems.

MO 11.4 Wed 15:15 N 25

triggering excitation energy transfer in molecular aggregates via nanoparticle near-fields — ●XIAOMENG LIU¹, LENNART SEIFFERT¹, THOMAS FENNEL¹, THOMAS NIEHAUS², and OLIVER KÜHN¹ — ¹Institut für Physik, Universität Rostock, D-18051 Rostock, Germany — ²Institute Lumière Matière, Université Lyon 1, F-69622 Villeurbanne CEDEX France

Laser-driven quantum dynamics has been studied for an organic-inorganic hybrid system consisting of a metal nanoparticle (NP) and a dye aggregate. The latter was described using approximate time-dependent density functional theory [1], i.e. by explicitly solving the time-dependent Kohn-Sham equations for the molecule driven by the total field. Polarization effects between the spherical NP and the molecules were described self-consistently, via high-order multipole expansion [2]. The structure of the near-field and its dependence on the distance and orientation of the aggregate was investigated in detail for the examples tetracene and JC-1 chloride. It was observed that the polarization effects have only minor influence on the electronic structure of the molecule. However, a strong effect is observed for laser excitation of the hybrid system. Here, the total electric field including the near NP's near-field is capable of enhancement and local triggering of excitation energy transfer, which has been described by means of a quantum master equation [3]. [1] T. A. Niehaus et al., Eur. Phys. J. D 35, 467 (2005); [2] L. Seiffert et al., Appl. Phys. B 121, 101 (2016); [3] V. May and O. Kühn. Charge and Energy Transfer Dynamics in Molecular System (Wiley-VCH, Weinheim 2011)

MO 11.5 Wed 15:30 N 25

Tuning nonradiative lifetimes via molecular aggregation — ALAN CELESTINO and ●ALEXANDER EISFELD — MIPPKS, Dresden, Germany

We show that molecular aggregation can strongly influence the nonradiative decay (NRD) lifetime of an electronic excitation. As a demonstrative example, we consider a transition-dipole-dipole-interacting dimer whose monomers have harmonic potential energy surfaces (PESs). Depending on the position of the NRD channel (q_{nr}), we find that the NRD lifetime (τ_{nr}^{dim}) can exhibit a completely different dependence on the intermolecular-interaction strength. We observe that (i) for q_{nr} near the Franck-Condon region, τ_{nr}^{dim} increases with the interaction strength; (ii) for q_{nr} near the minimum of the monomer excited PES, the intermolecular interaction has little influence on τ_{nr}^{dim} ; (iii) for q_{nr} near the classical turning point of the monomer nuclear dynamics, on the other side of the minimum, τ_{nr}^{dim} decreases with the interaction strength.

[1] arXiv:1611.09115 [physics.chem-ph]

MO 11.6 Wed 15:45 N 25

Optical Spectroscopy on Single Dye Crystals — ●CHRIS REHHA-GEN, STEFFEN WOLTER, and STEFAN LOCHBRUNNER — Universität Rostock, Institut für Physik, 18051 Rostock

Optical properties of dye crystals are of rising interest in applications, especially due to potentially large exciton mobilities. Furthermore, crystals provide stable and regular structures which are well suited for common characterization methods. Small crystals in the range of 10-500 μm are prepared from solutions of the dyes TTBC (1,1',3,3'-tetraethyl-5,5',6,6'-tetrachlorobenzimidazolocarbo-cyanine) and Coumarin 153. To investigate their optical properties we implement a microscope with a resolution of 40 μm for single-crystal absorption and fluorescence spectroscopy. The setup is combined with a streak-camera and can also be inserted in a femtosecond pump-probe experiment. First results indicate, that there is a connection between the macroscopic structure of the crystals and their optical properties. Especially some TTBC crystals show fluorescence spectra with components typical for J-type aggregation. The resulting increase in spectral overlap of absorption and

fluorescence implies enhanced exciton migration according to Förster theory.

MO 11.7 Wed 16:00 N 25

Growth and characterization of NbSe₂ on Al₂O₃ (0001) using molecular beam epitaxy — ●AVANINDRA KUMAR PANDEYA, KAI CHANG, ILYA KOSTANOVSKIY, and STUART PARKIN — Max Planck Institute of Microstructure Physics

The most common way to produce transition metal dichalcogenide (TMDC) thin films is via mechanical exfoliation, a method which is not well-suited to fabricate heterostructures with coherent interfaces or large-area thin film applications. Moreover, spintronic effects such as spin transfer torque are extremely sensitive to the quality of the heterointerface. Our approach is to use molecular beam epitaxy (MBE) to grow in-situ TMDC heterostructures and assess the layer and interface quality using in-situ characterization (RHEED, LEED, XPS and STM). Employing a two-step growth scheme, we achieved high-quality, single-crystalline NbSe₂ layers on Al₂O₃ (0001) substrates. A superconducting transition was observed below 4K and is found to be driven by the carrier density in the metallic layers. The achievement of epitaxial, high-quality TMDC layers with high spin-orbit coupling opens up good prospects to realize an efficient spin transfer in TMDC/ferromagnet bilayers.

MO 11.8 Wed 16:15 N 25

Casimir glue: Strong van der Waals adhesion of a poly-

mer film on rough substrates — JULIANE KLATT¹, PABLO BARCELLONA¹, ROBERT BENNETT¹, OLGA BOKAREVA², HAGEN FETH³, ANDREAS RASCH³, PATRICK REITH³, and ●STEFAN YOSHI BUHMANN^{1,4} — ¹Institute of Physics, University of Freiburg, Germany — ²Institute of Physics, University of Rostock, Germany — ³TrueDyne Sensors AG, Reinach, Switzerland — ⁴Freiburg Institute for Advanced Studies, Germany

Casimir-van der Waals dispersion forces have been shown to be responsible for the ability of geckoes to stick to very smooth and dry surfaces [1]. The effect has since lead to the fabrication of a biomimetic sticky tape [2]. Inspired by these developments, we propose that chemically inert and mechanically flexible polymeric films can enhance van der Waals forces in a similar way.

For the van der Waals adhesion of an ethylene-chlorotrifluoroethylene film on rough metal and dielectric substrates, we present a model that combines microscopic quantum-chemistry simulations of the polymer response functions and the equilibrium monomer-substrate distance with a macroscopic quantum-electrodynamics calculation of the Casimir force between the polymer film and the substrate. We predict adhesive forces up to 2.3 kN/mm², where the effect is reduced by substrate roughness and for dielectric surfaces.

[1] K. Autumn *et al.*, Proc. Natl. Acad. Sci. USA **99**, 12252 (2002).

[2] A. K. Geim *et al.*, Nature Materials **2**, 461 (2003).

MO 12: Posters 2: Molecular Dynamics, Clusters, and High Resolution Spectroscopy

Time: Wednesday 17:00–19:00

Location: P OGs

MO 12.1 Wed 17:00 P OGs

Photoionization of Ne₂: localized or delocalized? — HENDRIK SANN¹, ●ABIR MHAMDI², FLORIAN TRINTER¹, MARKUS SCHÖFFLER¹, PHILIPP V. DEMEKHIN², TILL JAHNKE¹, and REINHARD DÖRNER¹ — ¹Institut für Kernphysik, Universität Frankfurt, Frankfurt am Main, Germany — ²Institut für Physik, Universität Kassel, Kassel, Germany

We provide conclusive experimental evidence that for the van der Waals dimer Ne₂, a proper post-selection of photoelectrons yields electron angular distributions which are of well-defined parity [1]. This post-selection can be achieved for 2p-ionization by detecting the fragmentation of the Ne₂⁺ into Ne⁺+Ne, and it is possible because the potential energy curve ²Σ_g⁺ is the only dissociating state of Ne₂⁺(2p⁻¹). The electron angular distribution for this dissociative state, measured by the COLTRIMS [2] technique, is symmetric with respect to the direction to which the charged fragment is emitted. The present observations are supported by ab-initio electronic structure and dynamics calculations which were carried out by the Single Center method and code [3]. We conclude that the picture of localization or delocalization of a single particle or hole in this many-body wave function is oversimplified. In coincidence experiments on molecular ionization, one has to carefully discuss what is veritably measured and to which basis this measurement projects set the few-body wave function just as in any coincidence measurement on entangled photons.

References: [1] H. Sann, *et al.*, Phys. Rev. Lett., in press (2016). [2] R. Dörner, *et al.*, Physics Reports **330**, 96 (2000). [3] Ph. V. Demekhin, *et al.*, Journal of Chemical Physics **134**, 024113 (2011).

MO 12.2 Wed 17:00 P OGs

Collective resonances in dilute vapors — ●LUKAS BRUDER, ULRICH BANGERT, MARCEL BINZ, and FRANK STIENKEMEIER — Physikalisches Institut, Universität Freiburg

We have developed a phase-modulated pump-probe method which allows for efficient isolation and detection of multiple-quantum coherence signals. With this, we observed for the first time higher-order collective resonances in dilute atomic vapors [1]. The origin of these signals is debated since interatomic interactions are small in these systems [2]. Recently, we have significantly improved the spectral resolution in our setup (~1 GHz) and characterized the phase signature of the observed resonances. This revealed a phase characteristic depending on the fundamental hyperfine states. Our results have triggered interest from several theory groups currently working on an explanation of this phenomenon.

[1] L. Bruder, M. Binz, and F. Stienkemeier, Phys. Rev. A **92**, 053412

(2015).

[2] S. Mukamel, J. Chem. Phys. **145**, 41102 (2016).

MO 12.3 Wed 17:00 P OGs

A Velocity Map Imaging setup to benchmark technologies enabling the study of new systems on ion-molecule reactions — ●PATRICK STRÜBIN, FRANZISKA KRAMMER, TIM MICHAELSEN, JENNIFER MEYER, ATILAY AYASLI, BJÖRN BASTIAN, and ROLAND WESTER — Institut für Ionen und Angewandte Physik, Universität Innsbruck, Austria

Our group studies the dynamics of ion-molecule reactions by crossed-beam Velocity Map Imaging (VMI) [1]. For neutral reactions there have been a lot of investigations on the influence of excited vibrational states prior to the reaction [2]. We are planning to extend this research to ion-molecule reactions. As a first step a new crossed-beam VMI setup has been built. It will be used for measurements to determine the fraction of molecular excitation in the neutral molecular beam by a tunable optical parametric oscillator laser.

Furthermore we will extend our research to metal ion reactions with hydrocarbons. To produce metal ions we will use a laser vaporisation source [3,4] attached to the VMI spectrometer. Here we present test measurements and design considerations for the new VMI spectrometer, the metal ion source and the laser excitation scheme.

[1] R. Wester, Phys. Chem. Chem. Phys. **16**, 396 (2014)

[2] K. Liu, J. Chem. Phys. **142**, 080901 (2015)

[3] T. G. Dietz *et al.*, J. Chem. Phys. **74**, 6511 (1981)

[4] D. Proch and T. Trickl, Rev. Sci. Instrum. **60**, 713 (1989)

MO 12.4 Wed 17:00 P OGs

Coinage bimetallic complexes display ultrafast multiexponential electronic dynamics in an ion trap and in solution — ●FLORIAN BÄPPLER¹, SEBASTIAN KRUPPA², YEVGENIY NOSENKO², ROLF DILLER¹, and CHRISTOPH RIEHN^{2,3} — ¹Department of Physics — ²Department of Chemistry, TU Kaiserslautern — ³Forschungszentrum OPTIMAS, 67655 Kaiserslautern

Bimetallic coinage metal complexes of type [Me₂(dcpm)₂]²⁺, 1²⁺, (Me= Ag, Au; dcpm = bis(dicyclohexylphosphino)methane) are stabilized by metal-metal interactions and give rise to interesting optical properties for OLEDs, photocatalysis, and sensory applications. Their excited state dynamics have been investigated in parallel in gas phase by femtosecond photo-induced dissociation and in solution by transient absorption. Both studies report a multiexponential electronic decay after excitation of metal-centered states modulated by solvent molecules and counter ions.

MO 12.5 Wed 17:00 P OGS

Collinear Phase-modulated Femtosecond Pump-Probe Experiments Using a Low Repetition-rate Laser System — ●MARCEL BINZ, LUKAS BRUDER, ULRICH BANGERT, and FRANK STIENKEMEIER — Institute of Physics, University of Freiburg, Germany

A particularly robust and very versatile stabilization method for coherent time-resolved spectroscopy is the phase-modulation approach [1], [2]. The combination of continuous acousto-optical phase-modulation with lock-in detection greatly improves the signal-to-noise ratio and the sensitivity in this scheme. However, the method was thought to be suitable only for high repetition-rate laser systems ($\geq 200\text{kHz}$) which are not available in many labs.

Recently, we have successfully implemented this technique in a pump-probe scheme with fs laser pulses at 5kHz repetition-rate. We found that much higher modulation frequencies than laser repetition-rates can be used without losing performance. This effect, which we call phase-synchronous undersampling, shows promise for the implementation of the phase-modulation scheme in even lower repetition-rate XUV laser sources by shifting the carrier frequency far away from the low frequency noise spectrum.

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

[2] L. Bruder, M. Mudrich, and F. Stienkemeier, *Phys. Chem. Chem. Phys.* **17**, 23877 (2015).

MO 12.6 Wed 17:00 P OGS

Time-resolved XUV photoelectron spectroscopy of organic dyes in solution — ●JOHAN HUMMERT, IVGENII INKONNIKOV, NICOLA MAYER, MARTIN ECKSTEIN, and OLEG KORNILOV — Max-Born-Institut für nichtlineare Optik und Kurzzeitspektroskopie, Berlin

The electronic dynamics of organic molecules after photoexcitation are of great interest for biologically relevant systems as well as synthetic functional complexes. Often the environment, in many cases an aqueous solution, has a strong influence on the electronic structure. With the development of the liquid jet technique [1] methods demanding high vacuum conditions became applicable to molecules in solution.

The method employed here is time-resolved XUV photoelectron spectroscopy. Wavelength-selected high harmonics provided by a recently developed monochromator setup [2] are applied to probe the electronic relaxation of solvated molecules after single photon excitation with visible light. The high collection efficiency of a magnetic bottle spectrometer enables us to clearly distinguish molecular signals from strong solvent signals.

In a benchmark experiment with the water soluble dye "Quinoline Yellow WS" we measure ground state ionization energies and observe relaxation of excited states in solution. Excited state spectra and decay constants can be measured for concentrations down to 10mM, which establishes this technique for a wide range of samples.

[1] Faubel et. al., *J. Chem. Phys.* **106**, 9013-31 (1997)

[2] Eckstein et. al., *JPCL* **6**, 419-25 (2015)

MO 12.7 Wed 17:00 P OGS

Exploring Non-local Autoionization in Water Clusters and Aqueous Solutions — ●CLEMENS RICHTER¹, MARVIN N. POHL², CLARA SAAK⁴, MELANIE MUCKE⁴, EVGENY LUGOVY¹, ROBERT SEIDEL², EMAD F. AZIZ², BERND ABEL¹, BERND WINTER², and UWE HERGENHAHN^{1,3} — ¹Leibniz Institute of Surface Modification, Leibniz, Germany — ²Helmholtz-Zentrum Berlin, Berlin, Germany — ³Max-Planck-Institut für Plasmaphysik, Greifswald, Germany — ⁴Uppsala University, Uppsala, Sweden

Interaction of matter with ionizing radiation leads to emission of a multitude of electrons, either by direct photoemission or via secondary pathways, i.e. local and non-local autoionization. While the local Auger process is well established, the non-local processes intermolecular coulombic decay (ICD) and electron transfer mediated decay (ETMD) are topics of current research. Since both processes lead to the emission of low energy electrons - a primary source of radiation damage - we investigate autoionization in water and aqueous solutions of biological relevance. In our experiments electron-electron coincidence spectroscopy is performed using a magnetic bottle electron spectrometer. We present two examples of our current research on water-uracil clusters applying our newly constructed source for solvated biomolecule clusters as well as our first coincidence measurements of Li salt solutions using a liquid jet. While in the water-uracil clusters ICD is the predominant autoionization process. The Li salt

solutions unambiguously display an ETMD signature. Moreover, we discuss ETMD spectroscopy as potential tool for measuring contact ion pairs in solution.

MO 12.8 Wed 17:00 P OGS

Fluorescence dynamics and quantum yield measurements of a polycyclic tetrazolium compound in dependence on solvent viscosity — ●JAN-LUCAS WREE, TOM BOLZE, and PATRICK NUERNBERGER — Physikalische Chemie II, Ruhr-Universität Bochum, 44780 Bochum

The color change of tetrazolium salts that occurs during enzymatic reduction to formazans is exploited in applications like monitoring cell growth, since it can be conveniently measured in a quantitative fashion. Some particular tetrazolium compounds are known to further exhibit fluorescence, like the phenyl-benzo[c]tetrazolo-cinnolinium (PTC) which is investigated in this contribution.

We explore the fluorescence properties of PTC in alcoholic solvents whose viscosity span several orders of magnitude. Static measurements of absorption and fluorescence characteristics as well as of fluorescence quantum yields, measured against several reference compounds, are compared to the excited-state lifetimes obtained from time-correlated single-photon counting (TCSPC). The studies disclose that the emission characteristics vary but do not drastically change with solvent viscosity. This indicates that the emitting state is also deactivated by a competing, non-radiating reaction channel, but not by one that involves large intramolecular rotational motion, a process that would be strongly slowed down in more viscous solvents, as found for instance in molecular rotors or ultrafast C=C photoisomerization.

MO 12.9 Wed 17:00 P OGS

IR & UV/Vis spectroscopic studies on a luminescent heteroleptic mononuclear copper(I)-complex — ●MERTEN GRUPE¹, FABIAN DIETRICH², STEFAN BRÄSE³, MARKUS GERHARDS², and ROLF DILLER¹ — ¹Dept. of Physics, TU Kaiserslautern, 67663 Kaiserslautern — ²Dept. of Chem., TU Kaiserslautern, 67663 Kaiserslautern — ³Dept. of Org. Chem., KIT, 76131 Karlsruhe

Luminescence in copper-complexes is controlled by several photoinduced intra- and intermolecular processes, such as molecular flattening, intersystem crossing, solvation etc. For the elucidation of the underlying photophysics we employed femtosecond IR & UV/Vis transient absorption (TA) as well as transient anisotropy measurements and DFT calculations on a highly efficient luminescent heteroleptic mononuclear [1] copper(I)-complex. The results allow a rigorous comparison of the ultrafast dynamics in the UV/Vis spectral region with literature reports [2] [3] [4] on homoleptic copper(I)-complexes. Femtosecond IR TA facilitates an extended specification of the ultrafast processes in the heteroleptic mononuclear [1] copper(I)-complex.

[1] L. Bergmann et al. *Chem. Commun.*, 2013, 49 6501

[2] M. Iwamura et al. *Acc. Chem. Res.*, 2015, 48, 782-791

[3] G. B. Shaw et al. *J. Am. Chem. Soc.*, 2007, 129, 2147-2160

[4] Z. A. Siddique et al. *Inorganic Chemistry*, 2003, 42, 6366-6378.

MO 12.10 Wed 17:00 P OGS

Photophysics of porphyrin-based surface-anchored metal-organic frameworks investigated by time-resolved optical and EPR spectroscopy — ●MICHAEL ADAMS¹, ROWAN W. MACQUEEN², MICHAEL OLDENBURG¹, JAN BEHREND³, KLAUS LIPS², BRYCE S. RICHARDS¹, and IAN A. HOWARD¹ — ¹Institute of Microstructure Technology, Karlsruhe Institute of Technology — ²Berlin Joint EPR Lab, Helmholtz-Zentrum Berlin für Materialien und Energie — ³Berlin Joint EPR Lab, Fachbereich Physik, Freie Universität Berlin

Surface Anchored Metal Organic Frameworks (SURMOFs) are hybrid materials comprised of crystalline networks of organic molecules linking metal centers. The organic linkers may be active chromophores, and the structural order of the molecular assembly can give rise to intriguing new effects that differ from those observed in the lone chromophores. SURMOFs whose linkers are based on porphyrin chromophores have already stimulated interest due to their exhibition of photovoltaic action, and their ability to generate and transport triplet excitonic states to enable triplet-triplet annihilation upconversion. However, many fundamental questions regarding the photophysics of this system remain. In this contribution we provide a deeper insight into the SURMOF-2 structure using palladium porphyrin linkers by combining transient absorption spectroscopy (TAS), time-dependent luminescence and transient electron paramagnetic resonance (tEPR) measurements in order to elucidate the formation and transition be-

tween triplet, triplet aggregate, and radical species following photoexcitation.

MO 12.11 Wed 17:00 P OGS

Frequency conversion of organotetrelchalcogenide clusters — ●NILS W. ROSEMAN¹, JENS P. EUSSNER², EIKE DORNSIEPEN², STEFANIE DEHNEN², and SANGAM CHATTERJEE¹ — ¹Institute of Experimental Physics I, Justus-Liebig-Universität Giessen, Heinrich-Buff Ring 16, D-35392 Giessen, Germany — ²Faculty of Chemistry and Materials Sciences Center, Philipps-Universität Marburg, Hans-Meerwein-Straße, D-35043 Marburg, Germany

Cluster molecules based on organotin complexes do feature versatile properties. One of which is low-threshold nonlinear white-light generation [1]. This process is tentatively being assigned to the driven motion of delocalised electrons in the clusters ground state potential. To review this explanation, a systematic variation of the cluster components and correlation to the nonlinear response is crucial. Here, we present to nonlinear optical response of a series of organotetrelchalcogenide clusters based on the compound presented in [1]. Variation of the delocalised electron system is performed by changing the ligands, while the fundamental optical transition is changed by variation of the tetrel-moiety. Resulting in a drastic change of the nonlinear response; from white-light to second harmonic generation. [1] N. W. Rosemann et al., *A Highly Efficient Directional Molecular White-Light Emitter Driven by a Continuous-Wave Laser Diode*, *Science* **352**, 1301-1304 (2016)

MO 12.12 Wed 17:00 P OGS

Probing the anisotropic electronic structure of silicon cluster cations — ●MARKO FÖRSTEL, BERTRAM JAEGER, PHILIPP SPORKHORST, and OTTO DOPFER — Institut für Optik und Atomare Physik, Technische Universität Berlin, Hardenbergstrasse 36, D-10623 Berlin

Silicon is among the ten most abundant elements in our universe. In its ionic form it was found in the interstellar medium and even in the Earth's atmosphere. The Si^+ ion also plays a role in manufacturing processes of silicon based semiconductors. Here we set out to study the hitherto poorly understood fundamental chemistry and behavior of Si_n^+ ions. A recently updated tandem mass spectrometer coupled with a laser vaporization source [1] is utilized to study the molecular structure of $\text{Si}_n^+ - \text{Ar}_m$ cluster ions. Depending on cluster source conditions, we observe magic numbers in these systems that indicate structures which are strongly influenced by the anisotropic electron density of the central Si_n^+ ion. We describe the updated setup, present the experimental mass spectra and discuss the possible cluster structures underlying these magic numbers. Our discussion is supported by quantum chemical calculations.

[1] Photodissociation spectrum and structure of $\text{Au}_4^+ - \text{H}_2\text{O}$ clusters, Jaeger, B. K. A., Savoca, M., Dopfer, O., and Truong, N. X., *International Journal of Mass Spectrometry* (402) 2016.

MO 12.13 Wed 17:00 P OGS

XRD/SEM/EDX characterization of green synthesized silver nanoparticles — MIROSLAV CVETINOV¹, MAJA STOJANOVIC¹, MILOŠ BOKOROV¹, SLOBODAN GLISIC², and ●MILORAD ČAKIC² — ¹Faculty of Science, University of Novi Sad, Trg Dositeja Obradovića 4, Novi Sad, Serbia — ²Faculty of Technology, University of Nis, Bulevar Oslobođenja 124, Leskovac, Serbia

Due to the fact that silver nanoparticles (AgNP) exhibit broad spectrum of biocidal activity, they are often employed in industrial and consumer goods sectors. For the purpose of synthesis of green AgNPs, we used aqueous extract of *Fumaria officinalis* (earth smoke) obtained in alkaline solution resting for 5 days at room temperature (RT) as well as resting for 2 hours on boiling temperature of the reaction mixture (BT). Newly synthesized specimens were investigated by the methods of X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX). XRD confirmed crystallization of AgNP in face-centred cubic lattice (space group Fm-3m, lattice constant $a = 4.086 \text{ \AA}$). Using Scherrer equation on the most intense Ag peak in XRD spectra at Bragg angle $2\theta = 38.1^\circ$ we obtained average nanoparticle size of 21nm and 18nm for the RT and BT synthesized specimens, respectively. At specific points on specimen surface, EDX showed maximum Ag concentration of 44% and 81% for RT and BT synthesized specimens, respectively. This study presents convenient way to synthesize silver nanoparticles using plant materials. AgNPs obtained by this method show promising potential in drug formulations

production as well as in biomedical and agricultural applications.

MO 12.14 Wed 17:00 P OGS

Cryogenic Matrix Isolation FTIR Spectroscopy with Diamond Beam Splitter. — ●DMITRY STRELNIKOV¹, BASTIAN KERN², CHRISTOPH SÜRGER³, and MANFRED KAPPE¹ — ¹Physikalische Chemie, KIT, Karlsruhe, Germany — ²MPI for Solid State Research, Stuttgart, Germany — ³Physikalisches Institut, KIT, Karlsruhe, Germany

FTIR spectroscopy is a robust technique to obtain broad band spectra of various species. In case of valuable samples, which can be kept only at cryogenic temperatures and require long preparation time, one would like to measure in all accessible spectral regions. To extend the spectroscopic measurement range from Far-IR to near-IR a synthetic diamond beam splitter without compensator plate and UHV diamond viewports were installed in a Bruker IFS66v/S FTIR spectrometer. We have also modified the IR detector chamber to allow measurements with 5 different detectors. We demonstrate performance of the upgraded FTIR spectrometer by presenting measurements of matrix isolated fullerene ions and an adhesive tape.

MO 12.15 Wed 17:00 P OGS

IR spectroscopy of cationic nickel ethanol clusters - variation of cluster size and solvation shell — ●DANIEL BELLAIRE, MARKUS BECHERER, FABIAN DIETRICH, and MARKUS GERHARDS — TU Kaiserslautern, Fachbereich Chemie and research center OPTIMAS, Erwin-Schroedinger-Straße 52, 67663 Kaiserslautern

Clusters containing transition metals and aliphatic ligands provide model systems regarding e.g. catalytic properties, magnetism, reactivity and structure. Furthermore, investigation of clusters may reveal potential cooperative effects. Thus, the successive variation of size and ligand number of the metal clusters can give a fundamental insight. The investigated nickel clusters are produced by applying laser ablation to a rotating metal rod and by attaching the ethanol ligand(s) in a supersonic beam. The frequencies and frequency shifts of OH stretching vibrations (between different clusters) are probed by means of IR-photofragmentation spectroscopy. An assignment of structure and spin states is performed by comparing the experimentally observed vibrational frequencies with the calculated values obtained from DFT calculations.

Specifically, cationic $\text{Ni}_m(\text{ethanol})_n^+$ ($m=2-4$; $n=1-3$) clusters are spectroscopically investigated and explored by the aforementioned methods. The results give insight both into the structure and reactivity of the nickel aggregates.

MO 12.16 Wed 17:00 P OGS

High resolution spectroscopy on KCa — ●JULIA GERSCHMANN¹, ERIK SCHWANKE¹, HORST KNÖCKEL¹, SILKE OSPELKAUS¹, ASEN PASHOV², and EBERHARD TIEMANN¹ — ¹QUEST und Inst. f. Quantenoptik, Leibniz Universität Hannover — ²Sofia Universität "St. Kliment Ohridski", Bulgarien

The mixed alkali-alkaline earth molecules have recently attracted the interest of the scientific community due to possible applications in the field of cold and ultracold molecules. The combination of an alkaline and an alkaline earth atom leads to molecules which have permanent electric and magnetic dipole moments and thus offer manipulation of their states by external fields. Several ab initio calculations have been published on various combinations of a group IA and a group IIA atom from which one expects $2\Sigma^+ - 2\Sigma^+$ transitions in the near infrared. Experimentally, not so much is known about the molecular electronic states. The KCa molecules were created in a heatpipe oven and their thermal emission was recorded via a high resolution Fourier transform spectrometer. We have used laser induced fluorescence to assign the vibrational band heads of transitions from $v' \leq 2$ to $v'' \leq 3$ in the $2^2\Sigma^+ - 1^2\Sigma^+$ system. The resulting vibrational constants predicted other, moderately higher bandheads which can be observed in the emission spectrum. We are able to describe the rovibrational spectrum up to $N = 160$ of the $v = 0$ and $v = 1$ levels of the ground state of KCa. The rovibrational spectrum can be described by a Dunham series and one coefficient for the spin-rotation coupling. We will report on the status of the investigations.

MO 12.17 Wed 17:00 P OGS

High-resolution spectroscopy on the hyperfine structure of small aluminum-bearing molecules and analysis of their resulting electronic structures — ●BJÖRN WASSMUTH¹, ALEXANDER BREIER¹, GUIDO W. FUCHS¹, THOMAS F. GIESEN¹, and JÜRGEN

GAUSS² — ¹Institute of Physics, University of Kassel, 34132 Kassel, Germany — ²Institute of Physical Chemistry, University of Mainz, 55099 Mainz, Germany

We investigate metal-containing small molecules in the gas phase by means of millimeter/submillimeter-wave spectroscopy. The experimental investigation is guided by high-level quantum chemical calculations performed at Mainz.

Al¹⁶O, Al³²S, and Al³⁴S are produced by laser ablation of solid aluminum and a dilution of N₂O (2%) or H₂S (7%) in helium buffer gas, that subsequently undergoes an adiabatic expansion in our vacuum chamber. The resulting molecular beam is probed by monochromatic radiation in the frequency range up to 400 GHz. Measurements reveal the hyperfine structure of these linear molecules to follow Hund's case $b_{\beta S}$ coupling due to the nuclear spin of aluminum.

From the rotational constants the bond lengths are obtained. Analysis of our data including the hyperfine parameters of ALX (with $X \in \{F, Cl, Br, I\}$) reveals details of the respective electronic structures. With the present work new molecular parameters for future measurements on ALY (with $Y \in \{N, P\}$) are predicted.

MO 12.18 Wed 17:00 P OGs

Infrared spectroscopic investigations of N₂ adsorbed to cold Rhodium Iron alloy cluster cations — •MATTHIAS KLEIN, AMELIE EHRHARD, SEBASTIAN DILLINGER, JENNIFER MOHRBACH, and GEREON NIEDNER-SCHATTEBURG — Fachbereich Chemie and Forschungszentrum OPTIMAS, TU Kaiserslautern, 67663 Kaiserslautern, Germany

We investigated the N₂ adsorption behavior of bimetallic Rhodium-Iron cluster cations ($[Rh_lFe_m(N_2)_m]^+$), $l = n = 3 - 8$ and $m = 1 - 10$, and their geometric structures by means of InfraRed PhotoDissociation (IRPD) spectroscopy in comparison with DFT modelling. For $l = n = 3$ and 4 DFT suggests alloy structures, in case of $l = n = 4$ of high (D_{2d}) symmetry: N₂ adsorption and IRPD studies find strong evidence for preferential adsorption to Rh sites and mere secondary adsorption to Fe. The spectroscopic findings are well interpreted for the smaller clusters in terms of the computed structures, while the many details in the spectra of the larger clusters are subject of ongoing work.

MO 12.19 Wed 17:00 P OGs

Combined IR/UV investigations on isolated peptides: structural assignments for cyclic tetrapeptides — ANKE STAMM¹, •DOMINIQUE MAUÉ¹, KIRSTEN SCHWING¹, ASTRID SCHALY², STEFFEN SCHLICHER², JULIA BARTL², STEFAN KUBIK², and MARKUS

GERHARDS¹ — ¹TU Kaiserslautern, Dept. of Chemistry, Physical Chem. — ²TU Kaiserslautern, Dept. of Chemistry, Organic Chem., Erwin-Schrödinger-Str. 52/54, 67663 Kaiserslautern

Cyclopeptides are a widespread class of substances in nature with the antibiotic valinomycin being one of the most famous representatives. Their physiological effects are frequently based on the tendency to form bioactive conformations. Therefore the investigation of their structure is of great importance for understanding their functionalities. The mass- and isomer-selective combined IR/UV spectroscopy in molecular beam experiments represents a powerful tool for the structural investigation on isolated molecules in the gas phase. In combination with DFT calculations we are able to perform structural assignments for the electronic ground state. Here we present a structural determination for three different cyclic tetrapeptides, cyclo[L-Tyr(Me)-D-Pro-L-R-D-Pro] (R = Tyr(Me), Ala, Glu(Me)). A structural assignment with two intramolecular hydrogen bonds can be observed. Due to the asymmetric subunits there are different binding motifs within the cyclic tetrapeptide with R = Ala, Glu(Me) possible.

MO 12.20 Wed 17:00 P OGs

High resolution spectroscopy on LiSr — •ERIK SCHWANKE, JULIA GERSCHMANN, HORST KNÖCKEL, SILKE OSPELKAUS, and EBERHARD TIEMANN — QUEST und Inst. f. Quantenoptik, Leibniz Universität Hannover

The mixed alkali-alkaline earth molecules have recently attracted the interest of the scientific community due to possible applications in the field of cold molecules. These molecules have permanent electric and magnetic dipole moments and thus offer manipulation of their states by external fields. Several ab initio calculations have been published for LiSr from which one expects $^2\Sigma^+ - ^2\Sigma^+$ transitions in the near infrared. We have successfully recorded the near infrared spectrum of LiSr in a heatpipe oven. The thermal emission was recorded via a high resolution Fourier transform spectrometer. The assignment of the spectrum was facilitated by tuning a diode laser to an emission line, resulting in the observation of P-R-doublets and a simple vibrational progression in the fluorescence. Rotational constants from ab initio-calculations were used for a first guess of the rotational quantum numbers. Then we proceeded to take into account more transitions from higher rotational and vibrational levels. We are able to describe the rovibrational spectrum for the lowest vibrational states, deriving molecular parameters for the ground state $1^2\Sigma^+$. Perturbations due to couplings between the $2^2\Sigma^+$ state and the $1^2\Pi$ state have been observed and are used to investigate the $2^2\Sigma^+ - 1^2\Pi_{1/2}$ and $2^2\Sigma^+ - 1^2\Pi_{3/2}$ couplings. We will report on the status of the investigations.

MO 13: Probing Vibrations

Time: Thursday 11:00–13:00

Location: N 6

Invited Talk

MO 13.1 Thu 11:00 N 6

Ultrafast solvent fluctuations steer the hydrated excess proton in the Zundel cation H₅O₂⁺ — •FABIAN DAHMS¹, RENE COSTARD¹, EHUD PINES², EVA MARIA BRÜNING¹, TORSTEN SIEBERT¹, BENJAMIN P. FINGERHUT¹, ERIK T. J. NIBBERING¹, and THOMAS ELSAESSER¹ — ¹Max-Born-Institut für Nichtlineare Optik und Kurzzeitspektroskopie, Max-Born-Str. 2a, 12489 Berlin, Germany — ²Department of Chemistry, Ben Gurion University of the Negev, P.O.B. 653, Beersheva 84105, Israel

Hydrated protons are a key feature of biochemical systems. Not only do they mediate charge transport in aqueous environments but also play a key role in cell respiration. The Zundel cation represents a prototype species in which a proton is hydrated by two water molecules. By two-color femtosecond pump-probe measurements we were able to dissect the so-called Zundel infrared absorption continuum from the OH stretching and bending vibrations^[1]. In combination with theory, this led to a new picture where ultrafast solvent fluctuations modulate the position of the central H⁺ atom in the Zundel cation (H₅O₂⁺) causing the extreme broadening of infrared absorption. For the first time we investigate the dynamical behaviour of the O–H⁺–O proton transfer coordinate with femtosecond two-dimensional infrared spectroscopy. First results suggest ultrafast spectral diffusion, frequency shifts and vibrational lifetimes on a sub-100 fs time scale. In combination with results from pump-probe spectroscopy and theory, this gives new insight into vibrational motions of the hydrated proton itself. [1]:

Dahms, Fabian, et al., Angew. Chem. Int. Ed. 55 (2016): 10600.

MO 13.2 Thu 11:30 N 6

Ultrafast dynamics of interfacial water following UV photo-excitation of TiO₂ — SAMAN HOSSEINPOUR, SIMON SCHLEGEL, SHUMEI SUN, and •ELLEN BACKUS — Max Planck Institute for Polymer Research, Ackermannweg 10, 55128, Mainz

Hydrogen generation through photo-dissociation of water on the surface of TiO₂ has attracted profound attention over the past decades. Nevertheless, the molecular mechanism of the water splitting reaction has remained largely unresolved. The investigation of water during the water splitting reaction requires a surface sensitive tool which can probe the evolution of water molecules at the TiO₂ surface upon UV irradiation. In this study we exploit the inherent surface-sensitivity of sum-frequency generation (SFG) spectroscopy to probe the water molecules at the interface between bulk water and TiO₂. Femtosecond time-resolved SFG allows us to record changes in the orientation and hydrogen bonding interaction of interfacial water, as a function of the time following a UV pump pulse. Our preliminary results indicated a strong pH dependence of the relaxation/re-orientation of the water molecules after UV-irradiation of the TiO₂.

MO 13.3 Thu 11:45 N 6

The primary photochemical processes upon laser flash photolysis of a puckered ferrocyclobutadiene in liquid solution

studied by ultrafast femtosecond mid-infrared spectroscopy — ●BORIS WEZISLA, JÖRG LINDNER, and PETER VÖHRINGER — University of Bonn

The primary photoprocesses after laser flash excitation of the novel puckered ferracyclobutadiene, $[\text{Fe}\{\kappa^2\text{-C}_3(\text{NEt}_2)_3\}(\text{CO})_3]\text{BF}_4$, are explored using femtosecond time-resolved infrared spectroscopy in conjunction with extensive signal deconvolution and quantum mechanical computations, in an effort to fathom the possibility of utilizing this class of metallacyclobutadienes as efficient alkyne metathesis catalysts.

Signal deconvolution uncovers two short lived key intermediates for the primary substitution of a single CO ligand by an acetonitrile solvent molecule, which we already discovered in a previous study with nanosecond time-resolution [1]. These intermediates are assigned by comparison with DFT calculations to the triplet ground state of the precursor molecule and a formally octahedral, planarized ferracycle with an associated explicit solvent, respectively. By inclusion of the analytical solution of a kinetic model into the global fitting routine, reaction rates for elementary steps in the photochemical relaxation are determined, which explain the origin of the low and excitation wavelength dependent primary quantum yield of less than 25%.

[1] J. Torres-Alacan, B. Wezislá, M. Straßmann, A. C. Filippou, P. Vöhringer, *Chem. Eur. J.*, **2015**, *21*, 17184-17190.

MO 13.4 Thu 12:00 N 6

Effects of fractional charges on vibrational shifts of IR and Raman-active modes using Density Functional Theory — ●REYHANEH GHASSEMIZADEH¹ and MICHAEL WALTER^{1,2} — ¹Institute of Physics, University of Freiburg, 79104 Freiburg, Germany — ²Freiburg Center for Interactive Materials and Bioinspired Technologies (FIT), 79110 Freiburg, Germany

Organic molecules, such as polycyclic carbohydrates, are promising for future use in a new generation of solar cells. To investigate electronic structure and charge transfer characteristics of these molecules, we apply (Time-dependent) Density Functional Theory (TD-DFT).

In this work we focus on interactions between charge carriers and molecular vibrations in different carbon-based molecules with various intramolecular symmetries. Due to addition of fractional charges, our studies indicate, that vibrational frequencies $\omega(q)$ are changing compared to the natural species. We present the dependency of vibrational shifts of IR- or Raman-active modes on added fractional charges. An outlook about Raman-active vibrational shifts as finger print of charge transfer in donor-acceptor complexes in a common study with experimental collaborators is given.

MO 13.5 Thu 12:15 N 6

Study of the self-reaction products of benzyl radicals via IR/UV ion-dip-spectroscopy — ●FLORIAN HIRSCH¹, PHILIPP CONSTANTINIDIS¹, INGO FISCHER¹, and ANOUK M. RIJS² — ¹Institute of Physical and Theoretical Chemistry, University of Würzburg, Am Hubland, D-97074 Würzburg, Germany — ²Institute for Molecules and Materials, Felix Laboratory, Radboud University, Toernooiveld 7c, 6525 ED Nijmegen, The Netherlands

The self-reaction products of benzyl radicals produced by flash pyrolysis have been studied by ion-dip-spectroscopy in a free jet. Due to the high stability of this species and its great abundance in hot flames during combustion processes, these radicals might play an important role in the formation of polycyclic aromatic hydrocarbons (PAHs) and consequently soot. Because of the potential health and environmental impact of these undesired products, it is of significant importance to

understand the basic mechanisms which lead to these molecules in hot flames.

The spectroscopic method utilized in this study is capable of providing mass selective infrared spectra, which can be used for identification of the formed molecules. The radicals have been generated by flash pyrolysis from a nitrite precursor and ionized at fixed wavelengths at 265 or 275 nm. A tunable free electron laser provided infrared radiation in the range of 550 - 1750 cm⁻¹. Subsequent analysis of the differences in ion signals, with and without infrared excitation, resulted in the sought after infrared spectra for product identification.

MO 13.6 Thu 12:30 N 6

Enhancement of Vibrational Coherence by Excitation with Chirped Multipulses — ●ELISABETH BRÜHL, TIAGO BUCKUP, and MARCUS MOTZKUS — Physikalisch-Chemisches Institut, Ruprecht-Karls Universität Heidelberg, Germany

To steer photochemical reactions into selected channels, the tailoring of molecular vibrations is a fundamental control knob. Vibrational coherence of the ground state can be manipulated by using chirped pump pulses via intrapulse impulsive Raman scattering [1]. Additionally, electronic near-resonant excitation with multipulses has been shown to enhance vibrational coherence in the excited state [2]. In this work, these two methods of mode selective control are combined to study the interplay of chirped pulses and multipulses on vibrational coherence and population in the electronic excited as well as in the ground state over a range of excitation spectra. This is demonstrated by systematic phase shaping of the excitation pulse in transient absorption of dye molecules. Our control results of population and vibrational coherence show a strong dependence on the excitation detuning. For example, a blue-detuned multipulse enhances the vibrational coherence and its influence linearly adds to the one of the chirp. The effects for resonant and red-detuned excitation, on the other hand, are in general less pronounced and do not follow the same trend as for blue-detuned. For a better understanding of the underlying process and the assignment of ground and excited state contributions a numerical model is developed.

[1] Bardeen et al., JPC A 1998, 102, 17.

[2] Buckup et al., JPB 2008, 41, 074024.

MO 13.7 Thu 12:45 N 6

Distinguishing between silanol O-H and water O-H at the silica/water interface with time resolved SFG spectroscopy — ●JENÉE D. CYRAN¹, MICHAEL A. DONOVAN¹, JONATHAN F.D. LILJEBLAD², ERIC TYRODE², MISCHA BONN¹, and ELLEN H.G. BACKUS¹ — ¹Max Planck Institute for Polymer Research, Mainz, Germany — ²School of Chemistry, Division of Surface and Corrosion Science, Royal Institute of Technology, Stockholm, Sweden

The surface properties of silica in contact with aqueous solutions impact a plethora of fields, including geochemical, technological, and biological. Characterizing the silica/water interface on a molecular level is crucial for understanding the adsorption and reaction of water on the silica surface. Sum frequency generation (SFG) spectroscopy, a surface selective technique, affords the ability to use molecular vibrations to characterize the silica/water interface. The vibrational spectrum of this interface reveals a high-frequency feature centered at 3680 cm⁻¹. It has been debated whether this resonance originates from a free O-H from water or from a silanol (Si-O-H) group. Here, we use time- and polarization resolved SFG to distinguish between these two, as the water O-H can clearly reorient much faster than a surface-bound silanol group.

MO 14: Theory of Coupled Systems

Time: Thursday 11:00–13:00

Location: N 25

MO 14.1 Thu 11:00 N 25

Quantum dynamics of large molecular complexes using stochastic pure states — ●PANPAN ZHANG and ALEXANDER EISENFELD — MPIPKS Dresden

The Hierarchy of Pure States (HOPS)[1] is a stochastic method to efficiently solve non-Markovian open quantum system dynamics. It can also be used to calculate the linear [2] and nonlinear [3] spectra of molecular aggregates. Here we discuss the application of HOPS to these aggregates and present a new scheme how to truncate the hier-

archy, which allows to treat large systems with complex environments.

[1] D. Suess et al; Phys. Rev. Lett. 113, 150403 (2014) [2] G. Ritschel et al; J. Chem. Phys. 142, 034115 (2015) [3] P. Zhang and A.Eisfeld; J. Phys. Chem. Lett. 7,4488 (2016)

MO 14.2 Thu 11:15 N 25

Electron-phonon coupling with DFT — ●OLIVER STAUFFERT — Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str. 3, D-79104 Freiburg

We describe electronic structures for organic molecules, which are interesting for current research on organic solar cells, with time dependent density functional theory (DFT). Hereby we are especially interested in coupling of nuclear and electronic degrees of freedom. The most widely known occurrence of this coupling can be seen in the vibrational substructure of electronic spectra. These vibrational lines are described by the Franck Condon factors and can be calculated in a DFT framework. Results of simulations for polycyclic aromatic hydrocarbon show excellent agreements with the experimental data. We further investigate the influences of the environment, like a rare gas matrix and additional molecules on the vibrational degrees of freedom. Another consequence of electron phonon coupling can be seen in phonon assisted electron hopping. Conduction in organic systems is often described by electronic hopping in terms of a Hubbard Hamiltonian. The hopping parameter hereby depends on the distance of next neighbor atoms. Vibrations along the atomic axis can change the distance accordingly and enhance electronic hopping. This can lead to interesting new effects that we are investigating with DFT and an Su-Schrieffer-Heeger [1] model.

[1] W.P. Su, J.R. Schrieffer, and A.J. Heeger, Phys. Rev. Lett. 42, 1698 (1979)

MO 14.3 Thu 11:30 N 25

Towards a mobile solvent environment in quantum control optimizations — •DANIEL KEEFER and REGINA DE VIVIE-RIEDLE — Department Chemie, LMU München

Recently, we introduced an approach to explicitly include solvent molecules in quantum control optimizations [1]. The explicit environment was identified to have a significant influence on the relevant molecular properties. In a first approximation, movement of the solvent molecules was not considered during the quantum dynamical treatment of the reactant and the optimization of controlling laser pulses.

In our present study, we address this issue and extend our approach towards a fluctuating environment. The methodical techniques to achieve this will be presented, and the impact of mobile solvent molecules will be discussed on a molecular, synthetically relevant example.

[1] D. Keefer et al., *J. Phys. B* 48 (2015), 234003.

MO 14.4 Thu 11:45 N 25

Sub-picosecond Energy Transfer Mechanism with Highly Intense and Ultrashort THz Pulses — •PANKAJ KUMAR MISHRA^{1,2} and ROBIN SANTRA^{1,2,3} — ¹Centre for Free Electron Laser Science, DESY, Hamburg, Germany — ²The Hamburg Centre for Ultrafast Imaging, University of Hamburg, Germany — ³Department of Physics, University of Hamburg, Germany

With the advent of femtosecond lasers a couple of decades ago, ultrafast Temperature-jump experiments became possible and have since been used to study the very fast kinetics of fundamental steps in chemical reactions, folding processes in proteins and other biomolecules. Interestingly, T-jump experiments are also being used to study the fundamental aspects of the hydrogen bond dynamics and energy transfer in liquid water and other liquids in ultrashort timescales. We computationally investigated that one and half cycle, 141 fs long (fwhm) THz pulses spectrally centered at about 100 cm⁻¹ (3 THz) can transfer the large amount of energy to the liquid water, generating a T-jump of 700 K within less than a ps time-scale. Here, I will talk about the dynamics of ultrafast energy transfer from water clusters to bulk water by such THz pulses. I will present the mechanisms by which rotational and translational degrees of freedom of the water monomers gain energy from these sub-cycle pulses and discuss the ultrafast H-bond modification. Through their permanent dipole moment, water molecules are acted upon by the electric field and forced off their preferred H-bond network conformation.

MO 14.5 Thu 12:00 N 25

Kraftberechnungen in Spiropyran — •OLIVER BRÜGNER und MICHAEL WALTER — FIT Freiburger Zentrum für interaktive Werkstoffe und bioinspirierte Technologien, Universität Freiburg

Spiropyran sind photo- und mechanochrome Moleküle. Die ursprünglich farbneutralen Moleküle können sich durch Bestrahlung mit ultraviolettem Licht beziehungsweise durch mechanische Kräfte durch Brechung einer kovalenten Bindung in farbige Isomere mit dem Namen Merocyanin umwandeln. Die induzierte Verfärbung ist reversibel und die Entfärbung lässt sich z.B. durch ultraviolettes Licht induzieren. Diese erstaunliche Eigenschaft macht Spiropyran zu einem Stoff,

welcher für die Zukunft viele Anwendungen verspricht.

Mit dem langfristigen Ziel die mechanochromen Eigenschaften zu nutzen, um die Grundlage für die Herstellung von polymeren Kraftsensoren zu entwickeln, haben wir theoretische Untersuchungen basierend auf der Dichtefunktionaltheorie durchgeführt. Bestehende Methoden, um die Kraft zu berechnen, welche zur Verfärbung eines Spiropyranmoleküls benötigt wird, wurden von uns weiterentwickelt. Dabei ergibt sich, dass das Molekül für den Übergang nach Merocyanin zwei verschiedene Energiebarrieren überwinden muss. Die korrekte Bestimmung der benötigten Kraft verlangt die Betrachtung von zwei Reaktionskoordinaten und den zugehörigen Energiebarrieren. Berücksichtigung finiter Temperaturen bringt die berechneten Kräfte in Einklang mit dem Experiment [Gos].

[Gos] Gregory R. Gossweiler, Tatiana B. Kouznetsova, Stephen L. Craig, *J. Am. Chem. Soc.* 137 (2015) 6148-6151

MO 14.6 Thu 12:15 N 25

Energetics of charge transfer excitations from DFT ground-state calculations — •ROLF WÜRDEMANN¹ and MICHAEL WALTER^{1,2,3} — ¹FMF, Universität Freiburg, Freiburg, Germany — ²FIT, Universität Freiburg, Freiburg, Germany — ³IWM, Freiburg, Germany

Charge transfer excitations (CTE) are of interest in photovoltaics, organic electronics and molecular and organic magnetism. The energetics of CTE can be calculated by linear response time dependent density functional theory (lrTDDFT) using range separated functionals (RSF).

Compared to ground-state calculations, the use of lrTDDFT is computational very demanding.

Applying Huzinaga's improved virtual orbitals from Hartree-Fock Theory, we present a way to calculate the energetics of CTE using RSF by means of DFT ground-state calculations.

MO 14.7 Thu 12:30 N 25

Impact of dipole dispersion forces on the spectroscopic properties of a molecule — •JOHANNES FIEDLER¹, SAUNAK DAS^{2,3}, MARTIN PRESSELT^{2,3}, MICHAEL WALTER^{1,4}, and STEFAN YOSHI BUHMANN¹ — ¹Institute of Physics, University of Freiburg, Germany — ²Institute of Physical Chemistry, University of Jena, Germany — ³Leibniz Institute of Photonic Technology, Germany — ⁴Fraunhofer Institute for Mechanics of Materials, Germany

In molecular systems, dipole forces play an important role in determining their physical properties, such as bond length, binding energy and the electromagnetic response of the whole aggregate. Their impact is investigated in recent experiments and theories [1,2]. One typically distinguishes forces may arising from permanent from those being due to induced dipole moments.

We investigate the influence of dielectric response of a particle in the presence of a second one, where the two interact via the London dispersion force. We present the results of a quantum optical description based on macroscopic quantum electrodynamics and compare them with results obtained from density functional theory [3]. In particular, we study how the impact of the second particle on the first depends on the interparticle separation and their mutual orientation.

[1] V.V. Gobre, A. Tkatchenko, *nature communications* 4, 2341 (2013).

[2] S.Y. Buhmann, *Dispersion forces I*, Springer (Heidelberg, Berlin) 2012.

[3] T.E. Shubina *et al.*, *J. Am. Chem. Soc.* 136, 10890 (2014).

MO 14.8 Thu 12:45 N 25

Scalable composition of many-body interactions with linear size, linear/logarithmic-depth quantum circuits — •MICHAEL KAICHER¹, FELIX MOTZOI², and FRANK K. WILHELM¹ — ¹Universität des Saarlandes, Saarbrücken, Deutschland — ²Department of Physics and Astronomy, Aarhus, Dänemark

We develop a generalized framework for constructing many-qubit operator strings in linear time, with exact decompositions given for Pauli strings, number-conserving strings, parity-conserving strings, many-control Toffoli gates, Unitary Coupled Cluster operations, and sparse matrix generators. To this end, we use nearest-neighbour chaining operations to iteratively increase string length, in combination with a dynamical decoupling gate sequence to undo any changes outside the support of the many-body string. Moreover, we show that such constructions can be exponentially sped up via parallelization, with linear number of ancillary scratch registers required when the operators are not full rank. The formalism is readily applicable to different kinds of interactions including, CNOT, XX , and $XX + YY$.

MO 15: Environment Controlled Processes

Time: Thursday 14:30–16:30

Location: N 6

Invited Talk

MO 15.1 Thu 14:30 N 6

Tracking electronic processes inside dense matter by luminescence — ●ANDRÉ KNIE — Universität Kassel, Institut für Physik und Center for Interdisciplinary Nanostructure Science and Technology (CINSaT)

Typically electronic processes are investigated by charged particle detection - very often by electron spectroscopy. The step from small ideal systems, e.g. atoms, molecules, or clusters, to dense (real life) systems is obstructed for those techniques due to the very short penetration depth (few nm) of the charged particles. Another approach is the detection of photons, with orders of magnitude larger mean free paths.

Here, it will be shown how we employ high-resolution luminescence spectroscopy to observe ultra-fast energy transfers, namely the interatomic Coulombic decay (ICD), in noble gas clusters and electronic processes of photo excited liquid water within a liquid microjet.

In noble gas clusters as prototypes for dense systems, the photon emission following the electronic process can be investigated from small to large clusters. The fingerprint of the ultra-fast ICD feature, which can be identified by excitation energy and decay times, shows dramatic trends upon transition from small (dilute) to large (dense) clusters. Another very dense sample with a major impact on our daily life is liquid water and the electronic processes occurring upon XUV irradiation. Due to their luminescence fingerprint, those processes and thereby liquid water itself could be tracked over vast distances, e.g. astronomical distances.

MO 15.2 Thu 15:00 N 6

Interatomic coulombic decay in macroscopic environments — ●JOSHUA LEO HEMMERICH, ROBERT BENNETT, and STEFAN YOSHI BUHMANN — Physikalisches Institut, Albert-Ludwigs-Universität Freiburg

Interatomic coulombic decay (ICD) [1] has been a subject of study for the last two decades. The process takes place when a subunit of a cluster is ionized by removal of an inner valence electron. If the energy of the resulting state lies beneath the double ionization threshold a second subunit can be ionized by exchange of a virtual photon. Using the framework of macroscopic quantum electrodynamics [2] and time-dependent perturbation theory we study this process in arbitrary material environments, e.g. near a conducting plate. We compare our results in free space with the asymptotic quantum chemistry results based on the non-retarded Coulomb interaction to elucidate the impact of retardation. Finally, we briefly comment on the influence of macroscopic dielectric bodies on the ICD process.

[1] L.S. Cederbaum, *et. al.* Phys. Ref. Lett. **79** (24) 1997

[2] S. Scheel and S. Y. Buhmann, *Acta Physica Slovaca* **58** (5) 2008

MO 15.3 Thu 15:15 N 6

Femtosecond spectroscopy of the solvated electron in liquid ammonia over a wide range of excitation energies — ●TIM VOGLER, JÖRG LINDNER, and PETER VÖHRINGER — Institut für Physikalische und Theoretische Chemie, Universität Bonn

We recently reported on the vertical and below-band-gap ionization of liquid-to-supercritical ammonia employing photolytical excitation energies E_g of 9.3 eV [1] and 6.2 eV [2], respectively. In these studies the so called escape probability, i.e. the fraction of solvated electrons that are able to escape from their parent molecule, was around 70% in the first case and only 5% in the latter one (at room temperature and a pressure of 300 bar). This dramatic change in dependence on E_g opens up a very attractive window for further investigations: While the previous work puts special emphasis on the quantification of the escape probability under varying thermodynamic conditions, we now determined its behavior as a function of the excitation energy E_g .

To do so we extended our femtosecond pump-probe-spectrometer with a tunable UV light source providing a wide and gapless range of excitation energies E_g from 6 eV to 12 eV, implying a two-photon dependence of the ionization mechanism as found in [1]. Finally, the experimental results can be interpreted with a model regarding the optical band gap of liquid ammonia, which is around 8.2 eV [2].

[1] J. Urbanek *et al.*, *J. Phys. Chem. B* **116**.7 (2012),

[2] J. Urbanek and P. Vöhringer, *J. Phys. Chem. B* **118**.1 (2013)

MO 15.4 Thu 15:30 N 6

Mean free path of slow electrons retrieved from velocity map imaging of aerosol particles — ●MAXIMILIAN GOLDMANN¹, BRUCE L. YODER¹, STAVROS AMANATIDIS¹, EGOR CHASOVSKIKH¹, LUKAS LANG¹, ANDRAS BODI², DAVID LUCKHAUS¹, and RUTH SIGNORELL¹ — ¹Laboratorium für physikalische Chemie, ETH Zürich, 8093 Zürich — ²Swiss Light Source, Paul Scherrer Institut, 5232 Villigen

Electron mean free paths are important quantities for a number of physico-chemical phenomena ranging from aerosol physics and chemistry to radiation damage of biological tissues. We introduce and apply a novel method to determine the electron mean free path of low energy electrons in solid and liquid materials by velocity map imaging photoelectron spectroscopy of neutral aerosol particles using vacuum ultraviolet light. We extract the electron mean free path by comparing experimental with simulated photoelectron velocity map images of aerosol particles. For the simulation, we use a detailed scattering model [1].

Experimental photoelectron spectra of potassium chloride nanoparticles [2], liquid water droplets [1], and liquid-coated nanoparticles are presented. These photoelectron images were recorded at the VUV beamline at Paul Scherrer Institute and by means of a home-built table-top laser system.

[1] R. Signorell *et al.*, *Chem. Phys. Lett.* **658**, 1 (2016).

[2] M. Goldmann *et al.*, *J. Chem. Phys.* **142**, 224304 (2015).

MO 15.5 Thu 15:45 N 6

Monitoring the proton-transfer dynamics of a super-photoacid in acetone — ●JOHANNES KNORR¹, BASTIAN GEISSLER¹, CHRISTIAN SPIES^{1,2}, BJÖRN FINKLER², GREGOR JUNG² and PATRICK NUERNBERGER¹ — ¹Physikalische Chemie II, Ruhr-Universität Bochum, 44780 Bochum — ²Biophysikalische Chemie, Universität des Saarlandes, 66123 Saarbrücken

Photoacidity, i.e., a molecule's higher tendency to release a proton after electronic excitation, caused by changes in the molecule's electronic distribution that in turn affect corresponding hydrogen bonds, is frequently encountered in aromatic alcohols capable of transferring a proton to a suitable acceptor [1]. In this study, we investigate an extraordinarily strong super-photoacid, namely tris(1,1,1,3,3,3-hexafluoropropan-2-yl)8-hydroxypyrene-1,3,6-trisulfonate [2,3] in the aprotic solvent acetone—an environment which has not been addressed in previous time-resolved studies with other photoacids due to their weaker proton-transfer capabilities. In-depth analysis of time-correlated single-photon counting and femtosecond transient absorption experiments allows us to disclose solvation dynamics and radiative relaxation processes, as well as to derive a reaction scheme comprising the relevant steps of proton transfer along with the characteristic time scales.

[1] T. Förster, *Naturwissenschaften* **36**, 186 (1949)

[2] C. Spies *et al.*, *Phys. Chem. Chem. Phys.* **15**, 19893 (2013)

[3] B. Finkler *et al.*, *Photochem. Photobiol. Sci.* **13**, 548 (2014)

MO 15.6 Thu 16:00 N 6

An Experimental Test of Fermi's Golden Rule using Femtosecond IR Pump-Probe Spectroscopy — ●JEANNINE GLEIM, TOBIAS UNRUH, DENIS CZURLOK, JÖRG LINDNER, and PETER VÖHRINGER — Institut für Physikalische und Theoretische Chemie, Universität Bonn

Fermi's Golden Rule describes the coupling of an eigenstate of a quantum system with a resonant continuum of "background" states. In the context of vibrational energy relaxation in liquid solutions Fermi's Golden Rule (FGR) has never been tested rigorously through experimental studies. In the recent past, aqueous solutions of pseudohalide anions were used to study dynamical solute-solvent interactions and vibrational energy relaxation in hydrogen-bonded networks. Here, the cyanide stretching vibration of SC14N⁻, SC15N⁻, SeCN⁻ and OCN⁻ anions dissolved in water were studied with FTIR-spectroscopy as well as femtosecond IR-pump-probe spectroscopy. This solute vibration can couple resonantly to the continuum of bending-librational combination states of the liquid. All experiments were carried out under isobaric conditions at a pressure of 500 bar over a wide temperature range. T-dependent relaxation rates ($k(\text{VER})$) were determined from the decay of the $v = 1$ excited state absorption. Furthermore, the T-dependent

spectral overlap $S(T)$ between the solute and solvent absorption bands were determined independently and were used as a measure of the density of "background" states that enters Fermi's Golden Rule. According to FGR, a linear relationship between $S(T)$ and $k(\text{VER})$ exists which provides insight into the coupling strength of the solute and solvent.

MO 15.7 Thu 16:15 N 6

Photophysics and electrodynamics of indole and indole-water clusters — THOMAS KEIRSPER^{1,2}, MELBY JOHNNY¹, JOSS WIESE^{1,2}, SEBASTIAN TRIPPEL^{1,2}, and JOCHEN KÜPPER^{1,2,3} — ¹Center for Free Electron Laser Science (CFEL), Deutsches Elektronen Synchrotron (DESY), Hamburg, Germany — ²The Hamburg Center for Ultrafast Imaging, University of Hamburg, Germany — ³Department of Physics, University of Hamburg, Germany

The properties of atoms and molecules are strongly dependent on their

environment and hydrogen bonds are of universal importance in chemistry and biochemistry [1]. Therefore, it is highly desirable to bridge the gap between single, isolated molecules and molecules in solvation.

Here, we investigate the photophysics of a spatially separated pure sample of indole-water clusters, an amino-acid chromophore (indole) solvated by single water molecule [2]. The photofragmentation owing to 1s core hole ionization of indole's nitrogen were analysed with (photoelectron) photoion-photoion coincidence (PIPICO) maps. Indications for electron and proton or hydrogen atom transfer to the hydrogen bonded water molecule, as well as different Coulomb explosion channels, due to further emission of electrons on the indole-side of the cluster, were observed.

[1] A. L. McClellan, J. Chem. Educ., 44 (9), 547 (1967)

[2] Chang, Horke, Trippel, Küpper, Int. Rev. Phys. Chem. 34(4), 557-590 (2015)

MO 16: Posters 3: Experimental Techniques and Theoretical Approaches

Time: Thursday 17:00–19:00

Location: P OGs

MO 16.1 Thu 17:00 P OGs

Resolving Vibrational from Electronic Coherences in Two-Dimensional Electronic Spectroscopy: The Role of the Laser Spectrum — FRANCO V. DE A. CAMARGO¹, LENA GRIMMELSMANN^{1,2}, HARRY L. ANDERSON³, STEPHEN R. MEECH¹, and ISMAEL A. HEISLER¹ — ¹School of Chemistry, Norwich Research Park, University of East Anglia, Norwich NR4 7TJ, United Kingdom — ²Physical Chemistry II, Ruhr-University Bochum, 44780 Bochum, Germany — ³Department of Chemistry, Chemistry Research Laboratory, University of Oxford, Oxford OX1 3TA, United Kingdom

Light-induced coherent superposition of states are observed through the presence of oscillations in two-dimensional electronic spectroscopy (2DES). The pioneering 2DES studies on coherences mostly focused on single coordinates of the real part of 2D maps, with limited scanning of the waiting time, because of the long data acquisition times. Here we use a state-of-the-art 2D spectrometer that quickly acquires data with very good signal-to-noise to recover complex-valued 2DES maps and study vibrational coherences in a zinc-porphyrin monomer. Further we show that these signatures are critically dependent on the laser spectrum, demonstrating that a blueshift filters pathways so that the final result matches exactly those expected for an electronic coherence. This result is of crucial importance for the interpretation of coherences in 2DES. Finally, we use this new understanding of the laser spectrum effects to perform a complementary 2D experiment that lifts any ambiguity in the interpretation.

MO 16.2 Thu 17:00 P OGs

Two-dimensional Electronic Spectroscopy of Controlled Isolated Systems — ULRICH BANGERT, LUKAS BRUDER, MARCEL BINZ, DANIEL UHL, KATHARINA SCHNEIDER, ANDREAS WITUSCHEK, and FRANK STIENKEMEIER — Institute of Physics, University of Freiburg, Germany

Two-dimensional electronic spectroscopy (2DES) is a powerful tool to study coherences and correlations on ultrafast time scales. Until now, 2DES has been limited almost exclusively to condensed phase studies. Our aim is to apply 2DES to controlled isolated systems by using doped helium nanodroplet beams. Helium nanodroplets provide the dopant with a cold environment and minimal perturbation, which are ideal conditions to study the behavior of an individual system in a well-controlled environment.

However, the target density in doped helium droplet beams is several orders of magnitudes lower than in bulk condensed phase samples. We adapt a phase modulation technique [1] to overcome this issue. Using this, we currently implement a 2DES setup combined with a doped helium droplet beam. This setup will open exciting new possibilities for future 2DES studies.

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

MO 16.3 Thu 17:00 P OGs

The Stability of Broadband Phase Shaping in Liquid Crystal Spatial Light Modulators — ELISABETH BRÜHL, TIAGO BUCKUP, and MARCUS MOTZKUS — Physikalisch-Chemisches Institut, Ruprecht-Karls Universität Heidelberg, Germany

Liquid crystal spatial light modulators (LCM) have found many successful applications in physical chemistry, where they are used to modulate phase, amplitude and polarization of femtosecond (fs) laser pulses. In this regard, shot-to-shot as well as long-term modulation stability of LCMs are crucial requirements on its application in the broadband shaping of fs pulses. In this work, we show that when LCMs are applied to broadband tailoring of fs pulses (12 fs), depending on acquisition and detection conditions, noise figures up to 7 % can be observed. Our results show that spectral phase instability is originated by the LCM. In order to understand and thus minimize such instabilities, phase-sensitive measurements based on second harmonic generation of the tailored pulse, comparison of rapid-scan and step-scan results as well as careful control of the LCM temperature were implemented. The noise figure can be decreased by a factor of ten if a rapid-scan data acquisition approach is used instead of step scan. Furthermore, the study shows that the key in maximizing pulse stability and minimizing noise effects lies in careful control of the LCM operating temperature, improving the shot-to-shot stability of the output tailored pulse by a factor of two. Based on the experimental data we developed a physical model for a deeper understanding of the influence, especially the average scheme, and the level of noise.

MO 16.4 Thu 17:00 P OGs

Amplitude and phase shaping of femtosecond laser pulses in the ultraviolet with the help of an acousto optical modulator — SASCHA BICKHARDT, CRISTIAN SARPE, ALEXANDER KASTNER, PHILIPP HILLMANN, ARNE SENFTLEBEN, and THOMAS BAUMERT — University of Kassel, Institute of Physics and CINSaT, Heinrich-Platt-Str. 40, D-34132 Kassel, Germany

Femtosecond laser pulse shaping is the key technology in quantum control. So far, we were able to demonstrate pulse shaping with subcycle temporal accuracy making use of phase and amplitude modulation of femtosecond laser pulses in the infrared spectral region [1]. The experimental demonstration of molecular strong-field control schemes was achieved [2].

Organic molecules typically show pronounced absorption bands lying in the ultraviolet (UV) spectral region. Tailoring ultrashort UV laser pulses with respect to temporal and spectral shape opens up the possibility to investigate electron dynamics within different organic molecules, e.g. chiral ones.

We present the current status of our 4f and acousto optical modulator based setup for amplitude and phase shaping in the ultraviolet.

[1] J.Koehler *et al.*: *Optics Express* **19** (12), 11638-11653 (2011)

[2] T.Bayer *et al.*: *Physical Review Letters* **110**, 123003 (2013)

MO 16.5 Thu 17:00 P OGs

Optimization of data acquisition in time-domain spectroscopy experiments — DANIEL UHL, LUKAS BRUDER, MARCEL BINZ, ULRICH BANGERT, and FRANK STIENKEMEIER — Institute of Physics, University of Freiburg, Germany

We are exploring different approaches to optimize the data acquisition in time-domain spectroscopy, in particular, in phase-modulated pump-probe and 2D spectroscopy experiments. On the one hand, compressed sensing can be used to significantly reduce the amount of data points,

while yielding the same information content. This method allows in principle to go below the fundamental boundary of the sampling rate given by the Nyquist-Shannon-Theorem. On the other hand, we work on a software-based lock-in amplifier to improve data acquisition which represents a cost-effective alternative to commercial devices. This provides much higher flexibility: simultaneous detection with custom demodulators and filter algorithms is possible and acquisition times can be individually optimized for specific applications.

MO 16.6 Thu 17:00 P OGS

Development of a table-top soft X-ray source for probing ultrafast molecular dynamics — ●S. RAABE¹, G. GOLDSZTEJN¹, E.T. KARAMATSKOS², S. TRIPPLE², K. KOVÁCS³, E. BALOGH³, B. MAJOR³, V. TOSA³, J. KÜPPER², K. VARJÚ³, M.J.J. VRAKKING¹, and A. ROUZÉE¹ — ¹Max-Born-Institute, Max-Born-Str. 2A, 12489 Berlin, Germany — ²Center for Free-Electron Laser Science, DESY, Notkestr. 85, 22607 Hamburg, Germany — ³Department of Optics and Quantum Electronics, University of Szeged, Szeged, Hungary

High harmonic generation (HHG) is a powerful technique to generate ultrashort bursts of short-wavelength radiation. These pulses provide a way to capture ultrafast electronic and nuclear motion in matters with an exquisite temporal resolution down to the attosecond timescale. However, due to the low conversion efficiency of the HHG process at high photon energies, experiments have so far been limited to a photon energy range below 100 eV. We are currently developing a bright soft X-ray source making use of two-color HHG [1], where the first laser has a wavelength centered around 800 nm and the other laser is in the mid-infrared part of the spectrum. We will present the design of our table-top soft X-ray source that includes a new high gas pressure cell that will be used to generate water window harmonics using this two-color laser scheme. The source will be used together with a velocity map imaging spectrometer to perform time-resolved photoion and photoelectron spectroscopy and a soft X-ray spectrometer enabling transient absorption spectroscopy.

[1] B. Schütte, Optics Express, 23, 26 (2015)

MO 16.7 Thu 17:00 P OGS

Molecular processes with intense laser pulses — ●DENHI MARTÍNEZ^{1,2}, ALFONSO GUERRERO², IGNACIO ÁLVAREZ², THOMAS PFEIFER¹, ROBERT MOSHAMMER¹, and CARMEN CISNEROS² — ¹Max-Planck-Institut für Kernphysik, Saupfercheckweg 1, 69117 Heidelberg — ²Instituto de Ciencias Físicas, Universidad Nacional Autónoma de México, Av. Universidad s/n, Chamilpa, 62210 Cuernavaca, Morelos.

Through the interaction between strong laser fields and atoms or molecules, it is possible to elucidate the dynamical evolution in those systems. In the present work are shown some results for the dissociation and multiphoton ionisation processes of the nitromethane (CH₃NO₂) with V-UV radiation from laser pulses having nanoseconds pulse duration and at an intensity ranging from 10⁹ to 10¹⁰ W/cm². The observed ionic fragments were identified using high resolution mass spectrometry (Reflectron and TOF technique) and provide information on the fragmentation channel. We also present how to extend this research using a femtosecond laser providing higher intensity ranges and enabling therefore to study tunneling ionization. Moreover, femtosecond laser pulses, due to their timescale, allow to obtain a clearer picture of the electron dynamics the system. We combine this pump probe spectroscopy technique with a reaction microscope to determine the initial momenta of ions and electrons, based on the position and time of flight of their detection.

MO 16.8 Thu 17:00 P OGS

A molecular movie of Interatomic Coulombic Decay in NeKr — ●FLORIAN TRINTER¹, TSVETA MITEVA², MIRIAM WELLER¹, SEBASTIAN ALBRECHT¹, ALEXANDER HARTUNG¹, MARTIN RICHTER¹, JOSHUA WILLIAMS¹, AVERELL GATTON³, BISHWANATH GAIRE³, THORSTEN WEBER³, JAMES SARTOR⁴, ALLEN LANDERS⁴, BEN BERRY⁵, VASIL STUMPF², KIRILL GOKHBERG², REINHARD DÖRNER¹, and TILL JAHNKE¹ — ¹Institut für Kernphysik, Goethe-Universität, 60438 Frankfurt am Main, Germany — ²Theoretische Chemie, Physikalisch-Chemisches Institut, Universität Heidelberg, 69120 Heidelberg, Germany — ³Lawrence Berkeley National Laboratory, Chemical Sciences Division, Berkeley, California 94720, USA — ⁴Department of Physics, Auburn University, Auburn, Alabama 36849, USA — ⁵J. R. MacDonald Laboratory, Department of Physics, Kansas State University, Manhattan, Kansas 66506, USA

During the last 15 years a novel decay mechanisms of excited atoms has been discovered and investigated. This so called "Interatomic Coulombic

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

MO 16.9 Thu 17:00 P OGS

Fluorescence measurement of gas phase molecules by a single photon detector — ●SHARMILA SAIT, ALEXANDER KASTNER, PHILIPP SCHMIDT, ARNE SENFTLEBEN, THOMAS BAUMERT, ANDRE KNIE, ARNO EHRESMANN, and MARTIN PITZER — Institute for Physics and Center for Interdisciplinary Nanostructure Science and Technology (CINSaT), University of Kassel

Being one of the oldest techniques in molecular physics, fluorescence spectroscopy is broadly used and still advancing in a wide range of application. Time-resolved detection of single photons has over the last two decades become an established technique to study dynamics and solvent effects of biomolecules in solution. Nevertheless, obtaining a complete picture, i.e. spectral and polarization information, still requires scans or arrays of photomultipliers [1]. This poster highlights a novel, time efficient and portable setup for measuring the behavior of isolated molecules in gas phase. The synchrotron radiation is focused on the sample. Emitted fluorescence is passed through a Wollaston prism, diffraction grating and detected by a time and position sensitive single photon detector [2]. Consequently, polarization, wavelength and lifetime of fluorescence of each photon are recorded in a single measurement.

[1] Becker, et al., Microscopy Research and Technique 70, 403-409 (2007)

[2] A. Czasch et al., Nuclear Instruments and Methods in Physics Research A 580 (2007) 1066-1070

MO 16.10 Thu 17:00 P OGS

Implementation of a mechanical shutter into a He droplet apparatus using a hard disk drive actuator — ●KATHARINA SCHNEIDER — Institute of Physics, University of Freiburg, Germany

Controlled modulation or switching of light intensity is indispensable to many laser-based experiments. There are various ways to provide fast shuttering, varying in speed, reliability, expenses and extinction ratio.

Mechanical shutter excel in usability, expenses and transmission rate. Referring to [1], the voice-coil system of a computer hard disc drive can be modified to make a fast mechanical shutter, with switching times comparable to commercial devices. The voice-coil is driven by a custom circuit, using high-current pulses to ensure rapid shutter action. The direction of current is controlled by a TTL signal, enabling varying shutter frequencies and an asymmetric performance.

We setup such a shutter in a vacuum chamber to block a He droplet beam in front of a doping cell. This allows us to measure the remaining effusive signal in femtosecond HENDI (helium nanodroplet isolation) spectroscopy experiments. By subtracting this background from the measurement signal with the shutter open, the real doped droplet signal can be obtained.

[1] L. P. Maguire, S. Szilagy, and R. E. Scholten, Rev. Sci. Instrum. 75, 3077 (2004)

MO 16.11 Thu 17:00 P OGS

Natural chemical conversion and catalytic ortho/para conversion of the non-radioactive hydrogen isotopologues — ●BENNET KRASCH, ROBIN GRÖSSLE, SEBASTIAN MIRZ, and FLORIAN ALTENBRAND — Karlsruher Institute of Technology

Besides the chemical conversion processes an additional one exists for the homonuclear hydrogen isotopologues according to their relative nuclear spin orientation. There are two different species the so-called ortho hydrogen for parallel nuclear spins and the para hydrogen for antiparallel nuclear spins. These two species differ slightly in their thermodynamic properties as boiling point or specific heat capacity. The time constants for the natural chemical conversion is in the order of days to weeks in the gas phase. The ortho/para conversion time constant is in the order of thousand hours in the gas phase and ten hours in the liquid. At the Tritium Laboratory Karlsruhe (TLK) an analysis system has been developed to measure the isotopologue concentration in the liquid phase of a cryogenic distillation process, based

on infrared absorption spectroscopy. Since the ortho/para ratio has an influence on the IR spectra, it is indispensable to calibrate the system with catalytically produced ortho/para mixtures. Currently at the TLK an experiment has been installed to measure the time constants of catalytic conversion at a temperature range 70K-400K to determine the efficiency of the iron oxide used catalyst. A Laser Raman setup is used for a real-time analysis. This contribution presents first results of these measurements of the catalyst efficiency.

MO 16.12 Thu 17:00 P OGS

Progress on a Zeeman Slower for Molecules — ●MAURICE PETZOLD, PAUL KAEBERT, PHILIPP GERSEMA, MIRCO SIERCKE, and SILKE OSPELKAUS — IQO, Leibniz Universität Hannover, Hannover, Germany

Recently there has been great progress in laser cooling of molecules with quasi-diagonal Franck-Condon factors such as SrF CaF and YO. In particular, optical molasses, 2D- and 3D-magneto-optical traps have all been demonstrated. This is a tremendous step towards the creation of ultracold or even quantum degenerate samples of molecules via direct cooling techniques, extending the range of accessible molecules in the ultracold regime. Currently the molecule number in these traps is severely limited to $\sim 10^3$ due to the lack of high flux sources of molecules with velocities slow enough to be captured by magnetic or magneto-optical traps. Zeeman slowing, which is commonly used for atoms, is often thought to be impossible to implement for molecules due to the nature of the optical transitions used. Here we present a scheme of how to realize a Zeeman Slower for molecules. We simulate molecular trajectories emitted by a buffer gas cell and show that the slowing device provides significantly more flux of cold and slow molecules than other techniques used to date. The scheme is continuous and provides compression of the 1D-velocity distribution. We further report on progress on our demonstration experiment, which employs the proposed Zeeman slower scheme to Potassium atoms on the D1-line, an atomic system which exhibits many of the features and difficulties of molecular Zeeman slowing.

MO 16.13 Thu 17:00 P OGS

Cold collisions and slow reactions in a 22-pole trap — ●ERIC ENDRES, DANIEL HAUSER, OLGA LAKHMANSKAYA, STEFFEN SPIELER, GERHARD EGGER, MALCOLM SIMPSON, FABIO CARELLI, FRANCO GIANTURCO, and ROLAND WESTER — Institute for Ion Physics and Applied Physics, University of Innsbruck, Austria

Today the study of ion-molecule reactions moves towards cold chemistry which implies well controlled ion ensembles in a cold environment. A widely used tool to store and prepare ions by buffer gas cooling is a 22-pole rf ion trap [1].

For most applications it is important to know the translational and internal temperatures of the trapped ions. Here, we present detailed rotational state thermometry measurements over an extended temperature range for hydroxyl anions in different buffer gases and show incomplete rotational cooling of OH^- . Furthermore we present a method to manipulate and measure molecular quantum states by non-resonant photodetachment. Based on this we provide quantum scattering rate coefficients under full quantum state control for the rotationally inelastic collision of hydroxyl anions with helium [2]. Additionally, preliminary results of the influence of temperature on the inelastic collision rate are shown. Finally the exothermic proton transfer reaction $\text{D}^- + \text{H}_2 \rightarrow \text{HD} + \text{H}^-$ with a barrier of about 0.33 eV [3] is analysed. Here we investigate whether this reaction may occur at low temperature via tunneling through this barrier.

[1] R. Wester, J.Phys.(2009); [2] D. Hauser Nat.Phys.(2015); [3] E. Hauffler, J.Phys.Chem.(1997)

MO 16.14 Thu 17:00 P OGS

A novel spectroscopy technique for complex molecular ions in the gas phase — ●JÜRGEN GÖCK¹, KLAUS BLAUM¹, CHRISTIAN BREITENFELDT^{1,2}, ULRICH GRÖÖZINGER³, SEBASTIAN GEORGE¹, THOMAS HENNING³, HOLGER KRECKEL¹, SUNIL KUMAR S¹, CHRISTIAN MEYER¹, GAËL ROUILLE³, DMITRY STRELNIKOV⁴, and ANDREAS WOLF¹ — ¹Max-Planck-Institut für Kernphysik, Heidelberg, Germany — ²Institut für Physik, Ernst-Moritz-Arndt-Universität Greifswald, Greifswald, Germany — ³Max-Planck-Institut für Astronomie, Heidelberg, Germany — ⁴Institut für Physikalische Chemie II, Karlsruher Institut für Technologie, Karlsruhe, Germany

The origin of the diffuse interstellar bands (DIBs)[1] and the unidentified infrared emission bands (UIEs) are long-standing questions in the field of astrophysics. DIBs are interstellar absorption features in the

visible to near-infrared range, whereas the UIEs can be found in the emission spectra of astronomical objects. Complex molecular ions are candidates in particular since the first and only DIB carrier identified so far is the C_{60}^+ ion[2]. At the Max-Planck-Institut für Kernphysik we are developing a new technique for gas-phase spectroscopy of molecular ions that combines a cryogenic ion trap, which emulates the extreme conditions in the interstellar medium (10 K and 2000 particles/cm³), with extremely sensitive mid-infrared detectors. The experimental aim is to identify unknown carrier species of the spectral lines. The measurement scheme and the current status of the experimental setup will be presented. [1] Herbig, G. H., Annu. Rev. Astron. Astrophys. 33, 19-73 (1995). [2] Campbell, E. K. et al., Nature 523, 322-323 (2015)

MO 16.15 Thu 17:00 P OGS

Stochastic Wavepacket Approach to Modelling Penning Ionisation — ●ALEXANDER BLECH¹, DANIEL M. REICH¹, EDVARDAS NAREVICIUS², and CHRISTIANE P. KOCH¹ — ¹Universität Kassel, Deutschland — ²Weizmann Institute of Science, Rehovot, Israel

Cold Penning ionisation reactions of metastable helium display sharp tunneling resonances. In this regime the reactants can be described by a modicum of partial waves with one dominant one, when the collision energy matches a resonance [1,2].

Recently, the products of the Penning ionisation reaction have been detected using VMI. For Ar colliding with He*, an additional ring is observed which is absent for Kr. This situation can be attributed to the spin-orbit interaction. However, the angular dependence is more isotropic than one would expect. We therefore model the ionisation process using a stochastic wavepacket approach and calculate the cross section in the exit channels.

[1] Henson et al., Science 338, 234 (2012).

[2] Klein et al., Nat. Phys., doi:10.1038/nphys3904, (2016).

MO 16.16 Thu 17:00 P OGS

Three-body bound states induced by a p-wave resonant two-body interaction in 1D — ●LUCAS HAPP¹, MAXIM A EFREMOV^{1,2}, and WOLFGANG P SCHLEICH^{1,3} — ¹Institut für Quantenphysik und Center for Integrated Quantum Science and Technology (IQST), Universität Ulm, D-89081 Ulm, Germany — ²A.M. Prokhorov General Physics Institute, Russian Academy of Sciences, 119991 Moscow, Russia — ³Institute for Quantum Science and Engineering (IQSE), Department of Physics and Astronomy, Texas A&M University, College Station, TX 77843

The emergence of an infinite number of bound states in a system of three bosons, given the s-wave two-body binding energy is at the dissipation threshold, was first predicted by V. Efimov in 1970, and finally verified experimentally during the last decade. Since then, studies are exploring this effect in one- and two-dimensional systems, for different types of two-body interactions (long- and short-range) as well as symmetries of the underlying two-body resonance.

In this poster we present a system containing one light particle and two identical heavy ones, provided i) all particles move on a line, and ii) the heavy-light interaction potential has a p-wave (asymmetric) resonance. Within the Born-Oppenheimer approach we find the corresponding energy spectrum and the number of three-body bound states.

MO 16.17 Thu 17:00 P OGS

Correlated electron-nuclear dissociation dynamics: Classical versus quantum motion — ●JULIAN ALBERT, THOMAS SCHAUPP, and VOLKER ENGEL — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Emil-Fischer-Str. 42, 97074 Würzburg

We investigate the coupled electron-nuclear dynamics in a model system which undergoes dissociation. In choosing different initial conditions, the cases of adiabatic and non-adiabatic dissociation are realized. We treat the coupled electronic and nuclear motion in the complete configuration space so that classically, no surface hopping procedures have to be incorporated in the case that more than a single adiabatic electronic state is populated during the fragmentation. Concerning the highly anharmonic interaction potential, where it is expected that classical mechanics substantially deviates from quantum mechanics, it is found that the densities and fragmentation yields obtained from the two treatments are in astonishingly good agreement.

MO 16.18 Thu 17:00 P OGS

Transient wavepacket dynamics in excited-state potentials — MARKUS GÜHR and ●CARSTEN HENKEL — Universität Potsdam

Time dependent wavepacket dynamics driven by short laser pulses can

be simulated in two different ways. First, the static eigenstates of the system can be superposed with a spectral phase given by the excitation pulse. Second, a given static wavepacket can be propagated in the system's potential by solving the time-dependent Schrödinger equation.

Using molecular vibrational wavepackets, we illustrate that the two methods may deliver slightly different results at small propagation times and give an intuitive explanation based on causality. We point towards methods to verify the short-scale dynamics experimentally.

MO 16.19 Thu 17:00 P OGs

bound state properties of two dipoles in harmonic waveguides — ●GAOREN WANG¹, PANOGIOTIS GIANNAKEAS², and PETER SCHMELCHER¹ — ¹Zentrum für Optische Quantentechnologien, Universität Hamburg — ²Department of Physics and Astronomy, Purdue University

The bound states of two dipoles in a harmonic waveguide are investigated based on the local frame transformation (LFT) approach. Both the identical Bosonic and Fermionic dipoles are considered. In the weak dipole interaction regime, the length scale separation, which is the key prerequisite for the application of LFT approach, is verified by examining the wavefunction. Comparing the bound state energies obtained from LFT approach with the numerically accurate ones, it is found that, away from the threshold, the LFT approach with single partial wave approximation is accurate enough. Close to the threshold, higher partial wave states are strongly coupled, and more partial wave states should be incorporated in the LFT approach to obtain accurate results.

MO 16.20 Thu 17:00 P OGs

Generalization of the Davydov Ansatz — ●MICHAEL WERTHER^{1,2} and FRANK GROSSMANN¹ — ¹TU Dresden, Institut für Theoretische Physik, Zellescher Weg 17, 01069 Dresden — ²Max Planck Institute for the Physics of Complex Systems, Nöthnitzer Straße 38, 01187 Dresden

The Davydov Ansatz, originally introduced to study transport of biological energy in proteins by Davydov and co-workers^[1], is an efficient numerical tool for approximate solution of the Schrödinger-equation for different Hamiltonians. In recent works the D1-Ansatz has been successfully applied to the spin boson model as well as the Holstein molecular crystal model.^[2] For strong coupling the D1-Ansatz wave function can only insufficiently describe the dynamics of the system, according to its fixed phase space width. Here we propose an extension by adding a further degree of freedom which enables squeezing in phase space.^[3] The Dirac-Frenkel variational principle is applied to establish equations of motion for the parameters. First numerical results, executed for the prototype system with one oscillator, show a considerable improvement especially for strong coupling. This allows for an improved description of systems with many oscillators. As an outlook we present how the Davydov Ansatz can be used to include temperature effects into these models for strong coupling.

[1] A.S. Davydov, N.I. Kislukha, *Phys. Status Solidi B* 59 (1973) 465.

[2] K.-W. Sun et.al., *J. Chem. Phys.* 142 (2015) 212448

[3] F. Grossmann et.al., *Chem. Phys.* (2016), in press

MO 17: Experimental Techniques

Time: Friday 11:00–13:00

Location: N 6

Invited Talk

MO 17.1 Fri 11:00 N 6

Molecular-Frame Photoelectron Imaging of Controlled Complex Molecules — ●JOSS WIESE¹, SEBASTIAN TRIPPEL¹, 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

Since chemical function arises from the interplay amongst valence electrons, a view at the evolution of the highest occupied molecular orbitals (HOMOs) during a chemical reaction promises direct insight into the fundamentals of chemistry. We employ tomographic photoelectron imaging [1] of spatially controlled ensembles of indole and its 1:1 water complex strong-field ionised by intense near-infrared laser pulses. Reconstructed static three-dimensional photoelectron distributions in molecular-frame velocity space will be presented. These allow for the observation of the molecules' electron density distributions, photoelectron kinetic energies, and off-molecular-plane emission angles in 3D. The experimentally retrieved observables are discussed employing an extended strong-field approximation model. Those three observables provide a close glimpse at the laser-distorted HOMO potential surfaces of the investigated molecules in the gas phase and yield access to their changes in polarisability and dipole moment upon ionisation. Furthermore, the direct comparison of indole and its water complex allows inspection of the nature of hydrogen bonding in heteroaromatic biomolecules.

[1] Maurer, Dimitrovski, Christensen, Madsen, Stapelfeldt, *PRL* **109**, 123001 (2012)

MO 17.2 Fri 11:30 N 6

New pump-probe IToF setup to unravel ultra-fast photo conversion processes — ●MARIO NIEBUHR, DENNIS MAYER, TOM NEUMANN, AXEL HEUER, and MARKUS GÜHR — Institute for Physics and Astronomy, Uni Potsdam, Germany

Ultra-fast pump-probe spectroscopy of isolated molecules presents an important step towards understanding photo conversion processes and provides benchmark data for high-level ab-initio calculations. We are especially interested in photoisomerization systems such as azobenzene, and molecules, such as nucleobases, that are able to withstand energetic UV irradiation through very fast, non-ionizing and non-dissociating relaxation channels.

Our new setup utilizes time-of-flight mass spectroscopy to obtain delay dependent signals from excited state intramolecular conversion pro-

cesses with femtosecond time resolution. We use a commercial 100 kHz Yb:KGW system and its harmonics for pumping as well as probing. As the pulses for Yb based lasers are typically in the several 100 fs range, noncollinear parametric amplifiers (NOPAs) and fiber based spectral broadening are employed to access the sub hundred fs regime. First data of delay-dependent ion fragmentation yields will be presented.

MO 17.3 Fri 11:45 N 6

Broadband 7-fs 2D electronic spectroscopy by hollow-core fiber compression — ●XIAONAN MA, JAKUB DOSTÁL, and TOBIAS BRIKNER — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

Coherent two-dimensional electronic spectroscopy (2DES) is a powerful technique for resolving excited-state dynamics within coupled systems. To date, 2DES is mainly limited by laser bandwidth and peak-shape distortion (e.g. directional filtering) [1]. In this work, we combine a sub-7-fs supercontinuum generated in Ar-filled hollow-core fiber (HCF) with a diffractive-optic-based 2DES spectrometer for broadband 2DES measurement (500-700 nm) and reducing peak-shape distortion to a minimum [2].

We demonstrated the technique with cresyl-violet in ethanol. Measuring transient absorption in the same setup allow us to phase the 2DES data. The resulting peak-shape and quantum beating behaviour (585 and 2820 cm^{-1}) agree with a previous report [3]. We note that with sub-7-fs temporal resolution, our setup has the potential to observe extremely fast quantum beating (up to 3500 cm^{-1}), which is especially suited to investigate multi-chromophore systems with strong excitonic coupling. Meanwhile, this technique can be extended to even broader wavelength range (i.e. > 1 octave) or other regimes (i.e. UV and NIR).

[1] M. K. Yetzbacher *et al.*, *J. Chem. Phys.* **126**, 044511 (2007).

[2] X. Ma *et al.*, *Opt. Express* **24**, 20781 (2016).

[3] L. A. Bizimana *et al.*, *J. Chem. Phys.* **143**, 164203 (2015).

MO 17.4 Fri 12:00 N 6

Development of Cavity Ring-Down Spectroscopy for Carbon Isotope Analysis of Biomedical Samples — ●VOLKER SONNENSCHN¹, RYOHEI TERABAYASHI¹, HIDEKI TOMITA¹, NORIYOSHI HAYASHI¹, SHUSUKE KATO¹, LEI JIN¹, MASAHIITO YAMANAKA¹, NORIHIKO NISHIZAWA¹, ATSUSHI SATO², KOHEI NOZAWA², KENTA HASHIZUME², TOSHINARI OH-HARA², and TETSUO IGUCHI¹ — ¹Graduate School of Quantum Engineering, Dep. of

Engineering, Nagoya University, Nagoya, Japan. — ²ADME and Tox. Research Institute, Sekisui Medical, Tokai, Ibaraki, Japan

High sensitivity techniques such as Accelerator Mass spectrometry are commonly used for detection of the radioisotope ¹⁴C. In the environment, its abundance is typically at the ppt level, however in medical samples, where it is used as tracer isotope to study the metabolism of subjects or other biological processes, the abundance can be significantly higher. Detection may then be performed by application of optical methods such as Cavity Ring-Down Spectroscopy (CRDS), thus providing a more compact and inexpensive solution as well as possibilities for in-field measurements.

An overview and status of our current system for CRDS of ¹⁴CO₂ in the Mid-IR wavelength range will be given. The optical cavity is directly coupled to a CHNS elemental analyzer, allowing quick sample analysis. Thermo-electric cooling is applied to suppress interference by absorption of other close-lying molecular transitions. Remaining contaminants in biomedical samples are analyzed and the sensitivity and linearity of the ¹⁴C determination are estimated.

MO 17.5 Fri 12:15 N 6

Signal reversing cavity-based polarimetry: Measuring Chirality and Atomic Parity Nonconservation — ●ALEXANDROS K. SPILIO^{1,2}, DIMITRIOS SOFIKITIS¹, GEORGIOS E. KATSOPRINAKIS¹, and T. PETER RAKITZIS¹ — ¹Institute of Electronic Structure and Laser, Foundation for Research and Technology - Hellas, 71110 Heraklion, Greece — ²Department of Physics, University of Crete, 71003 Heraklion, Greece

Chirality is a fundamental property of life. Thus, chiral sensing and analysis is of fundamental importance in a number of scientific fields, ranging from pharmacology to fundamental physics and chemistry. The main constraint in the measurement of chiral signals is that they are typically very small and are thus limited by spurious birefringence and poor background subtraction procedures. Recently, our group has introduced a new cavity-based technique, which aims to overcome all these problems. The technique uses an optical cavity, which enhances the Optical Rotation (OR) signals by the number of cavity passes (typically ~1000). A number of signal reversals are incorporated in this method, which allow absolute measurements of chiral signals, without the need for background subtraction; the reversals suppress the spurious background birefringence, thus allowing the measurement of relatively small OR. This cavity-based setup has been proposed as a low-energy, table-top test of the Standard Model. It can be used for the detection of Atomic Parity nonconservation (PNC), to precisely

measure the cavity-enhanced parity-nonconserving OR of molecular transitions, in molecules such as Xe and Hg and I₂.

MO 17.6 Fri 12:30 N 6

Collinear rapid-scan two-dimensional spectroscopy via fluorescence detection with shot-to-shot phase cycling — ●SIMON DRAEGER, SEBASTIAN ROEDING, JAKUB DOSTÁL, and TOBIAS BRIXNER — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

We present pulse-shaper-assisted coherent two-dimensional (2D) electronic spectroscopy in liquids using fluorescence detection. A customized pulse shaper facilitates shot-to-shot modulation at 1 kHz and is employed for rapid scanning over all time delays. Phase cycling is used to extract the coherent information from the incoherent fluorescence signal. This enables us to obtain a full 2D spectrum with different nonlinear contributions in approximately 6 s measurement time (plus further averaging if needed). The method is applicable to various chemical systems. We employ cresyl violet in ethanol as a benchmark system.

MO 17.7 Fri 12:45 N 6

Time-dependent analysis of the mixed-field orientation of molecules without rotational symmetry — ●LINDA V. THESING¹, ROSARIO GONZÁLEZ-FÉREZ², and JOCHEN KÜPPER^{1,3,4} — ¹Center for Free-Electron Laser Science, DESY — ²Instituto Carlos I, Universidad de Granada — ³The Hamburg Center for Ultrafast Imaging, University of Hamburg — ⁴Department of Physics, University of Hamburg

We present a time-dependent study of the rotational dynamics of molecules without rotational symmetry and compute the 1D and 3D orientation in combined ac and dc electric fields. For a weak dc field, our results for the 1D orientation of a thermal ensemble of 6-chloropyridazine-3-carbonitrile (CPC) molecules are in good agreement with experimental observations for a state selected sample [1]. For an elliptically polarized laser, our theoretical results additionally show that the molecules are 3D oriented. If the dc field strength is increased, the 3D orientation is enhanced for certain angles between the ac and dc fields. Analyzing the field-dressed dynamics as the laser is turned on, we find highly non-adiabatic effects due to the complex energy level structure of the CPC molecule, and investigate their impact on the mixed-field orientation.

[1] Hansen et al., *J. Chem. Phys.* **139**, 234313 (2013)

MO 18: Biomolecules and Electron Transfer

Time: Friday 11:00–13:00

Location: N 25

MO 18.1 Fri 11:00 N 25

Ultrafast dynamics of the triazene compound Berenil — ●LENA GRIMMELSMANN, JOHANNES KNORR, CHRISTIAN SPIES, and PATRICK NUERNBERGER — Physikalische Chemie II, Ruhr-Universität Bochum, 44780 Bochum

Berenil is a versatile organic compound with a variety of applications, e.g. as the most widely used drug for treating the sleeping sickness in animals. Berenil efficiently binds to DNA, trypsin, and other biomolecules, but in all these cases it is reported to be a “non-fluorescent dye”. This points towards a very short excited-state lifetime and ultrafast nonradiative deactivation channels on which the molecule’s surrounding have a significant impact. Berenil comprises two amidinophenyl moieties linked by a triazene bridge, therefore it is chemically related to azobenzene but exhibits remarkable differences. In femtosecond fluorescence upconversion and transient absorption experiments, we disclose the ultrafast dynamics of berenil in various solvents, as well as berenil bound to trypsin, AT-rich DNA, and G-quadruplex DNA. Our results demonstrate that berenil exhibits an ultrafast deactivation of the S₁ state after photoexcitation, which we ascribe to associated molecular motion which does not require volume significantly beyond that occupied by the ground-state molecule. Studies in solvents with different viscosities substantiate these findings. As a general trend, one finds that the more restriction the binding introduces, the longer the fluorescence lifetimes. The transient absorption experiments provide additional insight into the nonradiative reaction channels and the possibility of photoisomerization.

MO 18.2 Fri 11:15 N 25

Characterization of Charge Separated States in (6-4)-Photolyase - Mechanistic Implications — ●MARA OSSWALD and BENJAMIN FINGERHUT — Max-Born-Institut für Nichtlineare Optik und Kurzzeitspektroskopie, Max-Born-Str. 2A, D-12498 Berlin

The UV irradiation of DNA causes the formation of cyclobutane pyrimidine dimers and of the (6-4)-photoproduct. The latter can be reverted by the enzyme (6-4)-photolyase. Triggered by light induced electron transfer, (6-4)-photolyase catalyzes the transfer of a hydroxyl group in addition to covalent bond cleavage. We present results on the effect of enzyme-electrostatics on the energetics of charge separated states in the (6-4)-photoproduct repair complex. Excited state calculations in gas phase and with enzyme were conducted using a QM/MM framework and TDDFT methods with modern long-range-corrected functionals as well as local coupled cluster linear response as ab-initio benchmark. By including all relevant molecules in the QM-region (ISO, ADE, (6-4)-lesion, His365, His369), the calculations account for the, up to date, largest QM-region regarding the (6-4)-repair complex. The results show that the electrostatics of the enzyme substantially affect the charge transfer (CT) states of the system. Most notably, the CT states from the isalloxazine ring to the (6-4)-lesion are destabilized and become inaccessible. While the (6-4)-photoproduct acts as electron acceptor in gas phase, a radical cationic state, arising from the reverted electron transfer direction, is favored once the enzyme is taken into account.

MO 18.3 Fri 11:30 N 25

Time-Resolved Measurement of Photoinduced Electron Transfer Processes in Perylene Diimides — ●ROBIN C. DÖRING¹, EDUARD BAAL², MALCOLM A. BARTLETT², CHRISTIAN PRINZISKY², REMCO W. A. HAVENITH^{3,4}, JÖRG SUNDERMEYER², and SANGAM CHATTERJEE^{1,5} — ¹Faculty of Physics and Materials Sciences Center, Philipps-Universität Marburg, Germany — ²Faculty of Chemistry and Materials Sciences Center, Philipps-Universität Marburg, Germany — ³Zernike Institute for Advanced Materials, Stratingh Institute for Chemistry, University of Groningen, The Netherlands — ⁴Ghent Quantum Chemistry Group, Department of Inorganic and Physical Chemistry, Ghent University, Belgium — ⁵Institute of Experimental Physics I, Justus-Liebig-Universität Gießen, Germany

Perylene derivatives form an important model system for studies of electron transfer (ET) in (molecular) donor-acceptor dye systems. Here, we introduce highly soluble perylene dihydrazides (PDH). We compare the PDH electron-transfer dynamics with a series of bisalkylperylene diimides. Time-resolved photoluminescence and photoluminescence excitation spectroscopy (PLE) measurements are performed. All samples show non-single-exponential decay dynamics. A rate-equation analysis including a shallow shelving state is able to reproduce the experimental data. Time-dependent density functional theory calculations of the triplet states supported by PLE measurements give evidence of rapid forward and reverse intersystem-crossing between the emissive and the triplet state.

MO 18.4 Fri 11:45 N 25

Quantum reaction control for quantum-limited biochemical magnetometers — ●KYRIACOS VITALIS and IANNIS KOMINIS — University of Crete, Department of Physics, Heraklion 71003 Greece

Radical-ion-pair reactions have triggered the study of quantum effects in biological systems. Here we address radical-pair reactions from the perspective of quantum metrology. Since the coherent spin motion of radical-pairs is effected by an external magnetic field, these spin-dependent reactions essentially realize a biochemical magnetometer. Using the quantum Fisher information, we find the fundamental quantum limits to the magnetic sensitivity of radical-pair magnetometers. We then find that the usual measurement scheme of reaction yields approaches the fundamental limits to within an order of magnitude. Finally, we demonstrate that with a realistic quantum reaction control reminding of Ramsey interferometry, here presented as a quantum circuit involving the spin-exchange interaction and a recently proposed molecular switch, we can approach the fundamental quantum limit within a factor of 2. This work opens the application of well-advanced quantum metrology methods to biological systems.

MO 18.5 Fri 12:00 N 25

Exploring Vibrational Dynamics of Anabaena Sensory Rhodopsin by Pump Impulsive Vibrational Spectroscopy — ●PARTHA PRATIM ROY¹, YOSHITAKA KATO², HIDEKI KANDORI², and TIAGO BUCKUP¹ — ¹Physikalisch Chemisches Institut, Ruprecht-Karls Universität Heidelberg, Germany — ²Department of Life Science and Applied Chemistry, Nagoya Institute of Technology, Japan

Anabaena Sensory Rhodopsin is a microbial retinal protein (MRP), which converts the photon energy to chemical energy by a cis-trans isomerization. Like other MRPs, it shows fast isomerization kinetics (<200fs) but surprisingly low quantum yield. Until now, it is not very clear which specific vibrational mode in excited potential energy surface (PES) drives such a fast isomerization kinetics. In this work, pump-impulsive vibrational spectroscopy with time resolution <20fs is utilized to capture the vibrational dynamics in ground and excited state and disentangle them. Excitation pulse (sub-13 fs), resonant with the ground-state absorption of the chromophore, is used for this experiment. The push and probe pulse (15 fs) were made resonant to absorption of K-product of the isomer. This study captures the vibrational signature in low frequency up to 2000 cm⁻¹. Strong ground state vibrational mode around 812, 1008 and 1539 cm⁻¹ was observed, which matches the spontaneous Raman spectrum of the molecule. Appearance of new vibrational modes around 900 and 1800 cm⁻¹ at certain push delay confirms their activity only in specific region of the excited state PES. This clearly shows the change of vibrational features from the FC-region to photoproduct region through the conical intersection.

MO 18.6 Fri 12:15 N 25

Laser-induced acoustic desorption of large molecules for

FEL experiments — ●ZHIPENG HUANG^{1,2}, DANIEL A. HORKE^{1,3}, MATTHIAS SCHUST¹, TIM OSSENBRÜGGEN¹, and JOCHEN KÜPPER^{1,2,3} — ¹Center for Free-Electron Laser Science, DESY, Hamburg — ²Department of Physics, University of Hamburg — ³Center for Ultrafast Imaging, University of Hamburg

Laser-induced acoustic desorption (LIAD) is a promising technique for gentle and efficient preparation of large intact neutral molecules into the gas-phase [1]. Here we demonstrate our newly set-up LIAD source, designed for prolonged measurement time, as required by FEL experiments, through automatic sample replenishment. Using a gas dynamic virtual nozzle we deposit a near-uniform layer of sample on a ~1 m long, 10 μm thick tantalum foil band. An acoustic wave was initiated by irradiating the backside of the foil with the third harmonic of a nanosecond Nd:YAG laser. The induced photoacoustic shock wave travels through the foil and desorbs samples into the gas-phase. A stable neutral phenylalanine plume was prepared and characterized using strong-field ionization by an intense femtosecond laser field with a linear time of flight mass spectrometer. Spatial-temporal profiles, velocity distributions of the LIAD plume as a function of desorption laser intensity were investigated. Its potential for applications in x-ray or electron diffraction imaging will be discussed.

[1] B. Linder and U. Seydel, *Anal. Chem.* **57**, 895 (1985)

MO 18.7 Fri 12:30 N 25

Momentum imaging of dissociative electron attachment in heterocyclic organic compounds — ●MARVIN WEYLAND¹, ALEXANDER DORN¹, XUEGUANG REN¹, HANS RABUS², and WOON YONG BAEK² — ¹Max Planck Institute for Nuclear Physics, Saupfercheckweg 1, 69117 Heidelberg, Germany — ²Physikalisch-Technische Bundesanstalt, Bundesallee 100, 38116 Braunschweig, Germany

Dissociative electron attachment (DEA) has been identified as a possible process for radiation damage. In short, DEA is a resonant two-step process in which first a low-energetic electron is captured by a molecule. The created negative ion can subsequently dissociate while the captured electron stays attached to one of the fragments. Detailed understanding of this reaction in biologically relevant molecules is crucial to improve its understanding. We investigated the heterocyclic organic compounds furan and pyridine as prototypes of typical organic molecules. Using a momentum imaging apparatus to detect the negative ions, we investigated the differential cross sections of several fragments after dissociation for each target molecule. From the resonance energy for formation of the fragment, combined with their kinetic energy and angular distributions, we can gain information about the dissociation process.

Our experimental results are compared to recent ab initio calculations with the goal to connect the dissociation process to specific electron scattering resonances in the target molecule.

MO 18.8 Fri 12:45 N 25

Individual Control of Lifetime and Triplet Yield in Halogen-Substituted Coumarin Derivatives — ●KATRIN OBERHOFER¹, MARTIN WÖRLE¹, MIKAYEL MUSHEGHYAN¹, SEBASTIAN WEGSCHEIDER¹, ROSITSA NIKOLOVA², REINHARD KIENBERGER¹, and HRISTO IGLEY¹ — ¹Physik-Department, Technische Universität München, James-Frank-Str., 85748 Garching — ²Faculty of Chemistry and Pharmacy, Sofia University, 1 J.Bourchier Blvd., 1126 Sofia, Bulgaria

Broadband transient absorption spectroscopy is utilized to examine lifetime and triplet yield in novel medicinally relevant Cl- and Br-substituted coumarin derivatives. Contradictory to the heavy-atom effect (HAE) absorption coefficient and fluorescent quantum yield for Cl-substituted compounds exhibit a strong enhancement. As DFT-calculations confirm several closely lying $\pi\pi^*$ and $n\pi^*$ states, we explain this behavior with an increased $\pi\pi^*$ character of the lowest emitting state, which overcompensates the HAE. Femtosecond pump-probe spectroscopy reveals lifetimes of 100 ps for Cl-, 20 ps for Br- and 40 ps for unsubstituted compounds in acetonitrile. In order to get a quantity for the intersystem-crossing rate we determined the relative triplet yield by the ratio of triplet-triplet and excited singlet absorption after thermalization. While the lifetimes correlate qualitatively with fluorescence quantum yields, attributed to the $\pi\pi^*$ increase, the triplet yield is significantly increasing with atomic weight of the substituted atom according to the HAE. Hence these two competing effects enable an independent control of lifetime and triplet yield.

MO 19: Clusters II (with A)

Time: Friday 11:00–13:00

Location: N 3

Invited Talk

MO 19.1 Fri 11:00 N 3

The Nanoplasma Oscilloscope — •CHRISTIAN PELTZ¹, A. LAForge², B. LANGBEHN³, R. MICHIELS², C. CALLEGARI⁴, M. DI FRAIA⁴, P. FINETTI⁴, R. SQUIBB⁵, C. SVETINA⁴, L. RAIMONDI⁴, M. MANFREDDA⁴, N. MAHNE⁴, P. PISERI⁶, M. ZANGRANDO⁴, L. GIANNESI⁴, T. MÖLLER³, R. FEIFEL⁵, K. C. PRINCE⁴, M. MUDRICH², D. RUPP³, F. STIENKEMEIER², and T. FENNEL¹ — ¹Uni Rostock, Germany — ²Uni Freiburg, Germany — ³TU Berlin, Germany — ⁴ELETTRA-Sincrotrone Trieste, Italy — ⁵Uni Gothenburg, Sweden — ⁶Uni Milan, Italy

Atomic clusters enable the well-controlled generation of nanoscale plasmas allowing for the study of their ultrafast light-induced correlated and collective dynamics. In particular, short-wavelength FELs can probe these dynamics in a regime that is fundamentally different from the well-known near-infrared domain. Plasma processes like collisional plasma heating, collective resonance excitation, and ionization avalanching that are generic in the NIR are strongly suppressed in the XUV and soft X-ray domain. Instead, sequential direct photo- or Auger emission dominates the plasma generation and heating dynamics. Signatures of this multistep ionization are characteristic plateau-like electron spectra and frustration of direct photo-emission by the cluster potential. Here we report the first direct time-resolved measurement of the underlying cluster potential evolution using the nanoplasma oscilloscope method, implemented in a recent two-color XUV pump-probe experiment at the seeded, high gain harmonic generation FEL FERMI FEL-2 operating in double stage mode.

MO 19.2 Fri 11:30 N 3

NIR-induced Auger decay in clusters — •BERND SCHÜTTE, MARC VRAKING, and ARNAUD ROUZÉE — Max-Born-Institut, Berlin

In nanoplasmas, which are formed by the interaction of clusters with intense laser pulses, Rydberg states are efficiently populated. While it is well known that some of the excited atoms and ions relax via the emission of photons [1], nonradiative relaxation mechanisms have only recently been discovered at moderate cluster ionization [2,3]. Here we show that nonradiative decay remains important at high ionization degrees, as is demonstrated for CH₄ clusters that interact with 400-fs NIR pulses ($I = 1 \times 10^{14}$ W/cm²). We observe a clear peak in the electron spectrum at 7 eV that is assigned to Auger decay, and that is explained by a 3-step process: (i) Our calculations show that the laser pulse removes almost all electrons from the outer shells of C, resulting in a dominant C⁴⁺ ion contribution at the end of the laser pulse. (ii) Rydberg and outer-vacancy shell levels are populated by recombination, and (iii) relax via Auger decay. This picture is consistent with a dominant C³⁺ ion contribution observed in the experiment, whereas, surprisingly, C⁺ and C⁴⁺ ion contributions are negligible.

Our results could explain the high average ion charge states that have been observed in clusters in spite of highly efficient recombination processes. Furthermore, the observed population inversion may be exploited for the development of an XUV or X-ray laser.

- [1] A. McPherson *et al.*, *Nature* **370**, 631 (1994).
- [2] B. Schütte *et al.*, *Phys. Rev. Lett.* **114**, 123002 (2015).
- [3] B. Schütte *et al.*, *Nat. Commun.* **6**, 8596 (2015).

MO 19.3 Fri 11:45 N 3

The 3D shapes of spinning helium nanodroplets — •B. LANGBEHN¹, Y. OVCHARENKO^{1,2}, D. RUPP¹, K. SANDER³, C. PELTZ³, A. CLARK⁴, R. CUCINI⁵, P. FINETTI⁵, M. DI FRAIA⁵, D. IABLONSKY⁶, A. C. LAForge⁷, V. OLIVER ÁLVAREZ DE LARA⁴, O. PLEKAN⁵, P. PISERI⁸, T. NISHIYAMA⁹, C. CALLEGARI⁵, K. C. PRINCE⁵, K. UEDA⁶, F. STIENKEMEIER⁷, T. FENNEL³, and T. MÖLLER¹ — ¹TU Berlin — ²European XFEL — ³Univ. Rostock — ⁴EPFL, Lausanne — ⁵Elettra-Sincrotrone Trieste — ⁶Tohoku Univ. Sendai — ⁷Univ. Freiburg — ⁸Univ. di Milano — ⁹Kyoto Univ.

Scattering techniques using intense femtosecond short-wavelength pulses from free-electron lasers (FEL) have been developed to gain an insight into the structure of nanoparticles such as viruses or clusters. Recent pioneering experiments in the hard X-ray range revealed that superfluid helium nanodroplets can gain high angular momentum resulting in large centrifugal deformation [1]. While hard X-ray experiments push towards atomic resolution, full 3D information on the particle shape (and orientation) from a single scattering pattern

requires access to the wide-angle scattering signal available only at longer wavelength [2]. We have used intense XUV pulses from the FERMI-FEL to retrieve the 3D shapes of single helium nanodroplets. We follow the evolution from axisymmetric oblate over triaxial prolate to two-lobed droplets with increasing angular momentum, as predicted by the theoretical model of a classical spinning drop.

- [1] Gomez *et al.*, *Science* **345** (2014)
- [2] Barke *et al.*, *Nat. Comm.* **6** (2015)

MO 19.4 Fri 12:00 N 3

Machine-learning assisted classification of diffraction images

— •J. ZIMMERMANN¹, M. SAUPPE¹, A. ULMER¹, B. LANGBEHN¹, S. DOLD², B. V. ISSENDORFF², I. BARKE³, H. HARTMANN³, K. OLDENBURG³, F. MARTINEZ³, K.H. MEIWE-BROER³, B. ERK⁴, C. BOMME⁴, B. MANSCHWETUS⁴, J. CORREA⁴, S. DÜSTERER⁴, R. TREUSCH⁴, T. MÖLLER¹, and D. RUPP¹ — ¹IOAP, TU Berlin — ²Univ. Freiburg — ³Univ. Rostock — ⁴FLASH@DESY

Short wavelength Free-Electron-Lasers (FEL) enable diffractive imaging of individual nanosized objects with a single x-ray laser shot. Due to the high repetition rate, large data sets with up to several million diffraction pattern are typically obtained in FEL particle diffraction experiments, representing a severe problem for the data analysis. We here propose a workflow scheme to drastically reduce the amount of work needed for the categorization of large data-sets of diffraction patterns, with the ultimate goal of developing an unsupervised training procedure. With a first supervised approach a classification and viewer tool is used for classifying manually selected high quality diffraction pattern. These patterns are then used as training data for a Residual Convolutional Neural Network (RCNN). The RCNN is designed for the classification of data for efficient indexing and subsequent analysis. The residual learning framework is a new type of network structure that drastically increases the depth of neural networks [He, *et al.* Deep Residual Learning, 2015]. First performance evaluations are done using data from a single-shot wide-angle scattering CDI experiment on silver clusters conducted in 2015 at the FLASH facility in Hamburg.

MO 19.5 Fri 12:15 N 3

The X-Ray Movie Camera: Time-Resolved Diffractive Imaging Of Individual Clusters

— •M. SAUPPE¹, T. BISCHOFF¹, K. KOLATZKI¹, B. LANGBEHN¹, M. MÜLLER¹, B. SENFFTELEBEN¹, A. ULMER¹, J. ZIMBALSKE¹, J. ZIMMERMANN¹, L. FLÜCKIGER², T. GORKHOVER^{1,3}, C. BOSTEDT^{4,5}, C. BOMME⁶, S. DÜSTERER⁶, B. ERK⁶, M. KUHLMANN⁶, D. ROLLES⁶, D. ROMPOTIS⁶, R. TREUSCH⁶, T. FEIGL⁷, T. MÖLLER¹, and D. RUPP¹ — ¹IOAP, Technische Universität Berlin, Germany — ²ARC CoAMI, LaTrobe University, Australia — ³LCLS, Stanford Linear Accelerator Center, USA — ⁴Argonne National Laboratory, USA — ⁵DoP, Northwestern University, USA — ⁶FLASH, Deutsches Elektronen-Synchrotron — ⁷optiX fab, Germany

Coherent diffractive imaging has been developed as a powerful technique for uncovering the structure of nano-sized particles like viruses, aerosols and clusters, as well as laser-induced nanoparticle dynamics. So far in time-resolved imaging experiments either optical pump lasers have been used or pump- and probe-images were superimposed. Here we present a new experimental setup, where the image of the initial particle and the image of final state are spatially separated and recorded by a two detector system. From the pump-image we can extract informations like size, shape and exposed intensity, from the probe-image we gain insight into light-induced dynamics. Probe pulses can be delayed up to 650 ps, realized by the new split-and-delay unit DESC, which has been permanently installed at the CAMP end-station at the FLASH FEL. First results will be discussed.

MO 19.6 Fri 12:30 N 3

Determination of average cluster sizes by fluorescence: proof of principle on Ne, Ar, and Kr clusters

— •XAVIER HOLZAPFEL¹, ANDREAS HANS¹, PHILIPP SCHMIDT¹, LTAIEF BEN LTAIEF¹, PHILIPP REISS¹, REINHARD DÖRNER², ARNO EHRESMANN¹, and ANDRÉ KNIE¹ — ¹University of Kassel, Institute of Physics and Center of Interdisciplinary Nanostructure Science and Technology (CINSaT), D-34132 Kassel, Germany — ²Institute of Nuclear Physics, J. W. Goethe University, D-60438 Frankfurt, Germany

Finite aggregates like clusters cover the range between molecular and

condensed matter physics and are used to study microscopic phenomena. The most important quantity for fundamental investigations of clusters is their average size. For clusters produced by a supersonic expansion, however, the average cluster size is usually estimated by an empirical law involving the stagnation pressure of the expansion, a law whose validity is under debate since its introduction. Here we present an alternative method for determination of the mean cluster size by resonant excitation of outer valence electrons and the subsequent emission of fluorescence photons in Ne, Ar and Kr. This method has been compared to average cluster size determination by the empirical law essentially corroborating the latter and can be used in the future for independent average cluster size determination.

MO 19.7 Fri 12:45 N 3

Signatures of Rabi cycling and excited state population in single-shot coherent diffractive imaging — •BJÖRN THORBEN KRUSE, CHRISTIAN PELTZ, and THOMAS FENNEL — Institute of Physics, University of Rostock, Germany

Single-shot coherent diffractive imaging (CDI) of individual free

nanoparticles enables the study of their three-dimensional shape and orientation [1] as well as their optical and electronic properties [2]. Recently, even signatures of quantum-mechanical vortices have been observed in scattering images of superfluid helium droplets [3], demonstrating that CDI provides access to the observation of rotational excitation in quantum liquids. Whereas the imaging of these vortices is an indirect detection of quantum effects, it remains an open question to what extent quantum effects can be observed directly and how their signatures would look like. Here we study the possibility to directly image the nonlinear quantum-mechanical few-level dynamics in laser-excited nanoparticles. For our theoretical analysis, we employ a Maxwell-Bloch type description of the scattering problem, where the polarization dynamics is described in local few-level approximation and field propagation is treated with the finite-difference time-domain method (FDTD). The origin of non-linear effects in resonant XUV scattering from droplets and possible routes to the spatiotemporal imaging of population dynamics will be discussed.

[1] I. Barke et al., Nat. Comm. **6**, 6187 (2015)

[2] C. Bostedt et al., Phys. Rev. Lett. **108**, 093401 (2012)

[3] L. F. Gomez et al., Science **345**, 6199:906-909 (2014)

MO 20: Clusters III (with A)

Time: Friday 14:30–16:30

Location: N 3

Invited Talk

MO 20.1 Fri 14:30 N 3

Experimental studies of Interatomic Coulombic Decay — •TILL JAHNKE — Goethe Universität Frankfurt, Institut für Kernphysik, Max-von-Laue-Str. 1, 60438 Frankfurt

Interatomic (or intermolecular) Coulombic Decay (ICD) has become an extensively studied electronic decay process during the last 15 years. Originally proposed by Cederbaum et al. [1] it was experimentally identified by means of different techniques [2,3,4] in the early 2000s. In ICD an excited atom or molecule deexcites by transferring its excitation energy to a loosely bound atomic neighbor and leads to the emission of an electron at that neighbor. Since that time a wealth of experimental and theoretical studies have shown that ICD is a rather common decay path in nature, as it occurs "almost everywhere" in loosely bound matter.

The talk will give a short introduction on ICD and report on recent experimental advances in the field covering time-resolved studies on the cluster size dependence of the efficiency of the decay and more detailed studies of different decaying systems.

[1] Cederbaum, L. S., Zobeley, J., and Tarantelli, F., Phys. Rev. Lett., **79**, 4778 (1997). [2] Marburger, S., Kugeler, O., Hergenbahn, U., and Möller, T., Phys. Rev. Lett., **93**, 203401 (2003). [3] Jahnke, T., Czasch, A., Schöffler, M. S., Schössler, S., Knapp, A. Käs, M., Titze, J., Wimmer, C., Kreidi, K., Grisenti, R. E., Staudte, A., Jagutzki, O., Hergenbahn, U., Schmidt-Böcking, H., and Dörner, R., Phys. Rev. Lett., **93**, 163401 (2004). [4] G. Öhrwall et al., PRL **93** 173401 (2004)

MO 20.2 Fri 15:00 N 3

Correlated decay processes in helium nanodroplets — •MARCEL MUDRICH¹, NIKOLAY SHCHERBININ¹, AARON LAForge¹, and ROBERT RICHTER² — ¹Physikalisches Institut, Uni Freiburg — ²Elettra Synchrotrone Trieste

Helium nanodroplets are commonly used as inert nanometer-sized cryo-matrices for spectroscopy of embedded atoms, molecules, and clusters. Upon irradiation with extreme-ultraviolet synchrotron radiation, though, ultrafast energy and charge exchange processes between embedded species and helium atoms or even among the helium atoms can occur. In this talk we give examples of such correlated decay processes: Interatomic Coulombic decay of pure helium droplets and Auger decay of embedded rare gas atoms.

MO 20.3 Fri 15:15 N 3

Laser initiation of the interatomic Coulombic decay process in quantum dots — •ANIKA HALLER¹, YING-CHIH CHIANG², MAXIMILIAN MENDER³, EMAD F. AZIZ^{1,4}, and ANNIKA BANDE¹ — ¹Helmholtz-Zentrum Berlin, Germany — ²The Chinese University of Hong Kong, Hong Kong — ³University of Pisa, Italy — ⁴Freie Universität Berlin, Germany

The interatomic Coulombic decay (ICD) has originally been predicted as ultrafast energy transfer process between atoms and molecules. Re-

cent studies show laser-induced ICD in paired quantum dots (QD) to be possible. We investigate a system of two GaAs QDs with two same-spin electrons each bound to one of the confining potentials. After resonant excitation of one electron by a time-dependent laser the system decays via ICD - interelectron energy transfer causes excitation of the other electron into the continuum. We show the field strength dependence of ICD from weak to strong-field intensities. The Fano peak profile shapes of the photoelectron spectra give a hint on the relative importance of ICD compared to the competing direct ionization. In addition, we study the impact of the laser focus. The electron dynamics is theoretically investigated by means of the space-resolved antisymmetrized multiconfiguration time-dependent Hartree method (MCTDH). As complementary approach we developed a state-resolved representation. We find multi-photon processes to be unimportant. Further, weak pulses display the highest ICD efficiency while direct ionization becomes less dominant. Focusing the laser on the light-absorbing QD further minimizes the probability for direct ionization.

MO 20.4 Fri 15:30 N 3

Time-resolved photoelectron spectroscopy on resonantly excited He nanodroplets — •A. C. LAForge¹, Y. OVCHARENKO², B. LANGBEHN², O. PLEKAN³, R. CUCINI³, P. FINETTI³, D. IABLONSKIY⁴, A. CLARK⁵, V. OLIVER ÁLVAREZ DE LARA⁵, P. FISER⁶, T. NISHIYAMA⁷, M. DI FRAIA³, C. CALLEGARI³, K. C. PRINCE³, K. UEDA⁴, F. STIENKEMEIER¹, M. MUDRICH¹, and T. MÖLLER¹ — ¹Universität Freiburg — ²TU Berlin — ³Elettra-Sincrotrone Trieste — ⁴Tohoku University, Sendai — ⁵EPFL, Lausanne — ⁶Università di Milano — ⁷Kyoto University

The ionization dynamics of helium droplets resonantly excited by intense, XUV radiation has been investigated. Depending on the intensity, the excited atoms can decay by interatomic Coulombic decay (ICD) or form a network of excited atoms which then collectively autoionize leading to nanoplasma formation [1,2]. Recently, we have extended our studies to time resolve the processes using a pump-probe technique. Using a UV laser to deplete the excited states, we observe a signal loss in the ICD signal in the photoelectron spectrum for short time delays followed by its reappearance at longer time delays (> 1 ps).

[1] Y. Ovcharenko et al., Phys. Rev. Lett. **112**, 073401 (2014)

[2] A. LaForge et al., Sci. Rep. **4**, 3621 (2014)

MO 20.5 Fri 15:45 N 3

Photoelectron elastic scattering probed by angle resolved X-ray photoemission from free SiO₂ nanoparticles — •BURKHARD LANGER, EGILL ANTONSSON, INA HALFPAP, JAQUELINE GOTTWALD, and ECKART RÜHL — Physikatische Chemie, Freie Universität Berlin

We report on measurements of the angular distributions of photoelectrons emitted from SiO₂ nanoparticles. A beam of free nanoparticles is crossed with a beam of X-rays from the BESSY II synchrotron facility. The studies were carried out over a wide energy range above

the Si 2*p* and O 1*s* absorption edges, respectively. The photoelectron angular anisotropy is found to be lower for photoemission from SiO₂ nanoparticles than the theoretical values for isolated Si and O atoms. This can be explained by elastic scattering of the outgoing electrons at neighboring atoms. We will discuss a simple model that allows us to determine the number of elastic scattering events. In addition, a Monte Carlo calculation using literature values for scattering cross sections can be applied to quantitatively describe the measured angular distributions.

MO 20.6 Fri 16:00 N 3

Tracing strong-field processes in nanoparticles in real time — •BERND SCHÜTTE¹, BJÖRN THORBEN KRUSE², CHRISTIAN PELTZ², MARC J. J. VRAKING¹, ARNAUD ROUZÉE¹, and THOMAS FENNEL^{1,2} — ¹Max-Born-Institut, Berlin — ²Universität Rostock

Strong-field ionization of solid-density targets is fundamentally different from strong-field ionization of atoms, and can result in highly efficient absorption of laser energy. In order to understand fundamental strong-field phenomena, the investigation of isolated nanoparticles is advantageous, as energy is not dissipated into the environment, allowing one to focus on the primary laser-matter coupling mechanisms.

Here we trace the charging of Ar and Xe nanoparticles directly in the time domain by applying the recently developed ionization ignition method [1]. Seed electron generation by an intense XUV pulse allows us to temporally control the heating and ionization induced by a 1.5-ps NIR pulse, whose intensity ($I = 1.5 \times 10^{13}$ W/cm²) is not sufficient to ionize neutral clusters. Surprisingly, we find that highly charged ions up to Xe¹⁵⁺ are produced. The average ion charge state increases exponentially during the rising edge of the NIR pulse, which is the first real-time observation of ionization avalanching. The experimental results will be compared with molecular dynamics calculations.

Our method provides new perspectives for the time-resolved investi-

gation of strong-field phenomena in nanostructures, liquids and solids. It could e.g. be used to record the ablation of material in real time, which is relevant for practical applications such as laser machining.

[1] B. Schütte *et al.*, Phys. Rev. Lett. **116**, 033001 (2016).

MO 20.7 Fri 16:15 N 3

Photo excitation of size selected lead clusters — •MARKUS WOLFRAM¹, STEPHAN KÖNIG¹, FRANKLIN MARTINEZ², GERRIT MARX¹, and LUTZ SCHWEIKHARD¹ — ¹Ernst-Moritz-Arndt Universität, Greifswald, Deutschland — ²Universität Rostock, Rostock, Deutschland

At ClusterTrap [1] the photodissociation of positively and negatively charged lead clusters has been investigated. In addition to monomer evaporation we observe a further decay mode: At intermediate sizes (Pbn⁺, n=19-25, Pbn⁻, n=16-31) the main fragmentation pathway is the breaking off of a neutral heptamer, Pb*7. After preliminary experiments with a Nd:YAG laser (532nm), we plan to extend the available photon energies by use of an OPO laser system. Furthermore, by electron impact ionization of stored metal cluster cations [2] and simultaneous storage of cluster anions and electrons in the Penning Trap [3] the production of cluster cations and anions, respectively, of higher charge states has been achieved. Thus, it will be possible to extend the current studies to multiply charged lead clusters where further decay pathways are expected. In this contribution, recent modifications of the experimental setup and first results on the photo-excitation of size selected mono-anionic and cationic lead clusters will be presented.

The project is funded by the Collaborative Research Center (SFB) 652.

[1] F. Martinez *et al.*, Int. J. Mass Spectrom. 365-366 (2014) 266 [2] L. Schweikhard *et al.*, Hyp. Int. 99 (1996) 97 [3] A. Herlert *et al.*, Phys. Scripta T80 (1999) 200