

## 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 PA 1.150 and PA 2.150; Poster Orangerie and Zelt West)

#### Invited Talks

MO 3.1	Mon	10:30–11:00	PA 2.150	<b>Electronic structure and relaxation of solvated organic molecules studied by time-resolved photoelectron spectroscopy</b> — JOHAN HUMMERT, GEERT REITSMA, NICOLA MAYER, EVGENII IKONNIKOV, MARTIN ECKSTEIN, ●OLEG KORNILOV
MO 5.1	Mon	14:00–14:30	PA 2.150	<b>Theoretical soft X-ray spectroscopy of transition metal compounds: A multi-reference wave function approach</b> — ●SERGEY I. BOKAREV
MO 5.5	Mon	15:15–15:45	PA 2.150	<b>Tracing the spatial and electronic structure of excited molecules using X-ray FEL and HHG light</b> — ●KIRSTEN SCHNORR
MO 8.1	Mon	16:15–16:45	PA 2.150	<b>Measurement of femtosecond dynamics in HCL molecules with THz streaking</b> — KATHARINA WENIG, MAREK WIELAND, SOPHIE WALTHER, ARNE BAUMANN, ANASTASIOS DIMITRIOU, MARK PRANDOLINI, OLIVER SCHEPP, IVETTE BERMUNDEZ MACIAS, MALTE SUMFLETH, NIKOLA STOJANOVIC, STEFAN DÜSTERER, JULIANE RÖNTSCH-SCHULENBURG, MARKUS DRESCHER, ●ULRIKE FRÜHLING
MO 12.1	Tue	14:00–14:30	PA 2.150	<b>Towards the study of quantum-state-selected Penning reactions</b> — JONAS GRZESIAK, SIMON HOFSSÄSS, VIVIEN BEHRENDT, FRANK STIENKEMEIER, MARCEL MUDRICH, ●KATRIN DULITZ
MO 16.1	Wed	14:00–14:30	PA 2.150	<b>Strong-field ionization of laser-aligned molecules</b> — ●JOCHEN KÜPPER
MO 18.1	Thu	10:30–11:00	PA 2.150	<b>Untersuchungen zur Coulomb-Wechselwirkung bei polyanionischen Metallclustern</b> — MADLEN MÜLLER, ●FRANKLIN MARTINEZ, NORMAN IWE, KLARA RASPE, STEFFI BANDELOW, JOSEF TIGGESBÄUMKER, LUTZ SCHWEIKHARD, KARL-HEINZ MEIWES-BROER
MO 20.1	Thu	14:00–14:30	PA 1.150	<b>Energy and charge transfer processes in helium nanodroplets</b> — ●MARCEL MUDRICH

#### Invited talks of the joint symposium SYPS

See SYPS for the full program of the symposium.

SYPS 1.1	Mon	14:00–14:30	RW HS	<b>Floquet engineering of interacting quantum gases in optical lattices</b> — ●ANDRÉ ECKARDT
SYPS 1.2	Mon	14:30–15:00	RW HS	<b>Experiments on driven quantum gas and surprises</b> — ●CHENG CHIN
SYPS 1.3	Mon	15:00–15:30	RW HS	<b>Exploring 4D Quantum Hall Physics with a 2D Topological Pumps</b> — ●ODED ZILBERBERG, MICHAEL LOHSE, CHRISTIAN SCHWEIZER, IMMANUEL BLOCH, HANNAH PRICE, YAACOV KRAUS, SHENG HUANG, MOHAN WANG, KEVIN CHEN, JONATHAN GUGLIELMON, MIKAEL RECHTSMAN
SYPS 1.4	Mon	15:30–16:00	RW HS	<b>Floquet Discrete Time Crystals in a Trapped-Ion Quantum Simulator</b> — ●GUIDO PAGANO, JIEHANG ZHANG, PAUL HESS, ANTONIS KYPRIANIDIS, PATRICK BECKER, JACOB SMITH, AARON LEE, NORMAN YAO, TOBIAS GRASS, ALESSIO CELI, MACIEJ LEWENSTEIN, CHRISTOPHER MONROE

## Invited talks of the joint symposium SYAD

See SYAD for the full program of the symposium.

SYAD 1.1	Tue	10:30–11:00	RW HS	<b>Integrated photonic quantum walks in complex lattice structures</b> — •MARKUS GRAEFE
SYAD 1.2	Tue	11:00–11:30	RW HS	<b>Testing the Quantumness of Atom Trajectories</b> — •CARSTEN ROBENS
SYAD 1.3	Tue	11:30–12:00	RW HS	<b>Engineering and probing topological bands with ultracold atoms</b> — •NICK FLÄSCHNER
SYAD 1.4	Tue	12:00–12:30	RW HS	<b>Statistical signatures of many-particle interference</b> — •MATTIA WALSCHAERS

## Invited talks of the joint symposium SYET

See SYET for the full program of the symposium.

SYET 1.1	Thu	11:00–11:30	RW HS	<b>The quantum design of photosynthesis</b> — •RIENK VAN GRONDELLE
SYET 1.2	Thu	11:30–12:00	RW HS	<b>On systems with and without excess energy in environment: ICD and other interatomic mechanisms</b> — •LORENZ CEDERBAUM
SYET 1.3	Thu	12:00–12:30	RW HS	<b>Molecular QED of Resonance Energy Transfer: Pair and Many- Body Theory</b> — •AKBAR SALAM
SYET 1.4	Thu	12:30–13:00	RW HS	<b>The Experimental Investigation of Interatomic/Intermolecular Coulombic Decay</b> — •UWE HERGENHAHN

## Invited talks of the joint symposium SYRP

See SYRP for the full program of the symposium.

SYRP 1.1	Fri	10:30–11:00	RW HS	<b>Attosecond seeding of high energy rescattered electrons</b> — •KENNETH SCHAFFER
SYRP 1.2	Fri	11:00–11:30	RW HS	<b>The molecular selfie - atomic-scale imaging with a single electron</b> — BENJAMIN WOLTER, MICHAEL G. PULLEN, ANH THU LEE, MATTHIAS BAUDISCH, KATHARINA DOBLHOFF-DIER, ARNE SENFTLEBEN, MICHAEL HEMMER, CLAUDIUS DIETER SCHRÖTER, JOACHIM ULLRICH, ROBERT MOSHAM- MER, STEFANIE GRÄFE, ORIOL VENDRELL, CHII DONG LIN, •JENS BIEGERT
SYRP 1.3	Fri	11:30–12:00	RW HS	<b>Multidimensional attosecond spectroscopy</b> — •NIRIT DUDOVICH
SYRP 1.4	Fri	12:00–12:30	RW HS	<b>Recollision-based high-harmonic generation from solids</b> — •GIULIO VAMPA

## Sessions

MO 1.1–1.6	Mon	10:30–12:30	K 1.011	<b>Attosecond Science I (joint session A/MO)</b>
MO 2.1–2.8	Mon	10:30–12:30	PA 1.150	<b>Biology Related Molecules</b>
MO 3.1–3.7	Mon	10:30–12:30	PA 2.150	<b>Photoelectron Spectroscopy</b>
MO 4.1–4.7	Mon	14:00–15:45	PA 1.150	<b>Photochemistry</b>
MO 5.1–5.5	Mon	14:00–15:45	PA 2.150	<b>X-Ray and XUV Spectroscopy (joint session MO/A)</b>
MO 6.1–6.5	Mon	16:15–17:45	K 2.016	<b>Atomic Clusters I (joint session A/MO)</b>
MO 7.1–7.6	Mon	16:15–17:45	PA 1.150	<b>High Resolution Spectroscopy</b>
MO 8.1–8.5	Mon	16:15–17:45	PA 2.150	<b>Ultrafast Spectroscopy with XUV (joint session MO/A)</b>
MO 9.1–9.8	Tue	14:00–16:00	K 2.016	<b>Atomic Clusters II (joint session A/MO)</b>
MO 10.1–10.6	Tue	14:00–15:45	K 2.019	<b>Strong laser fields - I (joint session A/MO)</b>
MO 11.1–11.8	Tue	14:00–16:00	PA 1.150	<b>Theoretical Approaches</b>
MO 12.1–12.6	Tue	14:00–15:45	PA 2.150	<b>Cold Molecules and Reactions (joint session MO/A)</b>
MO 13.1–13.21	Tue	16:15–18:15	Orangerie	<b>Posters 1: Ultrafast Spectroscopy</b>
MO 14.1–14.6	Wed	14:00–15:30	K 2.016	<b>Atomic Clusters III (joint session A/MO)</b>
MO 15.1–15.7	Wed	14:00–15:45	PA 1.150	<b>Complex Systems in the Gas Phase</b>
MO 16.1–16.6	Wed	14:00–15:45	PA 2.150	<b>Molecules in Intense Laser Fields (joint session MO/A)</b>
MO 17.1–17.19	Wed	16:15–18:15	Orangerie	<b>Posters 2: Cold Molecules and Clusters</b>
MO 18.1–18.6	Thu	10:30–12:15	PA 2.150	<b>Clusters IV (joint session MO/A)</b>
MO 19	Thu	12:30–13:15	PA 2.150	<b>Annual General Meeting of the Molecular Physics Division</b>
MO 20.1–20.6	Thu	14:00–15:45	PA 1.150	<b>Resonant Energy Transfer and Interatomic Coulombic Decay I</b>

---

MO 21.1–21.7	Thu	14:00–15:45	PA 2.150	<b>Advanced Time-Resolved Spectroscopy</b>
MO 22.1–22.20	Thu	16:15–18:15	Zelt West	<b>Posters 3: Experimental and Theoretical Techniques and High Resolution Spectroscopy</b>
MO 23.1–23.6	Fri	10:30–12:00	PA 1.150	<b>Resonant Energy Transfer and Interatomic Coulombic Decay II</b>
MO 24.1–24.7	Fri	10:30–12:15	PA 2.150	<b>Experimental Techniques</b>

### **Annual General Meeting of the Molecular Physics Division**

Thursday 12:30–13:15 PA 2.150

## MO 1: Attosecond Science I (joint session A/MO)

Time: Monday 10:30–12:30

Location: K 1.011

**Invited Talk**

MO 1.1 Mon 10:30 K 1.011

**Phase measurement and control with attosecond self-probing spectroscopy** — ●MICHAEL KRÜGER — Department of Physics of Complex Systems, Weizmann Institute of Science, Rehovot 76100, Israel

Attosecond spectroscopy is based steering electron dynamics by the electric field waveform of a strong laser field. High-harmonic generation (HHG), the mechanism underlying the production of attosecond pulses in the extreme ultraviolet (XUV), provides an in-built spectroscopic pump-probe measurement with extremely high spatial and temporal accuracy. The amplitude and phase of the emitted XUV radiation encodes all parts of the light-matter interaction in the recollision process, including ionization, propagation and photo-recombination. Here we present two applications of attosecond self-probing spectroscopy. In the first experiment, we initiate HHG with an XUV pulse instead of tunneling ionization, enabling us to measure and control the XUV photo-ionization dynamics in the presence of a strong infrared field in amplitude and phase [1]. In the second experiment, we compare HHG from two atomic species using linear XUV interferometry and extract the absolute difference in the photo-recombination dipole phase with high spatial resolution [2]. Our method gives access to hitherto inaccessible phase information, enabling attosecond control of HHG and tomographic reconstruction of the electronic structure of matter.

[1] D. Azoury et al., Nat. Comm. 8, 1453 (2017). [2] D. Azoury et al., manuscript in preparation (2017).

**Invited Talk**

MO 1.2 Mon 11:00 K 1.011

**Molecular Orbital Imprint in Laser-Driven Electron Recollision** — FELIX SCHELL, TIMM BREDTMANN, CLAUS PETER SCHULZ, SERGUEI PATCHKOVSKII, MARC VRAKING, and ●JOCHEN MIKOSCH — Max-Born-Institute, Max-Born-Strasse 2A, 12489 Berlin

Electrons released by strong-field ionization from atoms, molecules, or in solids can be accelerated in the oscillating laser field and driven back to their ion core. The ensuing interaction, phase-locked to the optical cycle, initiates the central processes underlying attosecond science. A key long-standing assumption regards the returning electron wavepacket as a plane wave. Here we study laser-induced electron rescattering associated with two different ionization continua in the same, spatially aligned, polyatomic molecule [1]. We show by experiment and theory that the electron return probability is in fact molecular-frame dependent and carries structural information on the ionized orbital. Pronounced deviations of the returning wavepacket from plane-wave character have to be accounted for in analyzing attosecond experiments based on strong laser fields.

[1] F. Schell, T. Bredtmann, C.P. Schulz, S. Patchkovskii, M.J.J. Vrakking, and J. Mikosch (submitted)

MO 1.3 Mon 11:30 K 1.011

**Valley-resolved Electronic Coherences in Silicon Observed by Attosecond Transient Absorption Spectroscopy** — ●MICHAEL ZÜRCH<sup>1</sup>, PETER M. KRAUS<sup>1</sup>, HUNG-TZU CHANG<sup>1</sup>, SCOTT K. CUSHING<sup>1</sup>, DANIEL M. NEUMARK<sup>1,2</sup>, and STEPHEN R. LEONE<sup>1,2,3</sup> — <sup>1</sup>Department of Chemistry, University of California, Berkeley, CA 94720, USA — <sup>2</sup>Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA — <sup>3</sup>Department of Physics, University of California, Berkeley, CA 94720, USA

Understanding the absorption of light and subsequent carrier dynamics in semiconductors plays a crucial role for optimizing next-generation photonic devices for increasingly faster performance. Here, attosecond transient absorption spectroscopy is employed for studying electronic coherences in single crystalline silicon during excitation by an intense 5-fs optical pulse. Transient absorption changes in the conduction band (CB) of silicon are monitored by an attosecond pulse at the silicon L-edge. In a frequency-over-energy Fourier analysis of the recorded transient absorption in comparison to the band structure coherences are identified. The data suggests that the optical pulse can coherently couple the valence band (VB) and CB at various critical points of the band structure. The time domain measurement allows measuring lifetimes of these coherences as well as their sequence of generation. The results provide insight into complex couplings between bands that take place during excitation with broadband ultrashort laser pulses, an effect that should be general for most semiconductor materials.

MO 1.4 Mon 11:45 K 1.011

**Light-Field-Driven Landau-Zener-Stückelberg Interferometry** — ●TAKUYA HIGUCHI and PETER HOMMELHOFF — Department Physik, Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), 91058 Erlangen

When electrons are placed under an optical field which is stronger than the internal field inside of a matter, their dynamics turn into non-perturbative regime. Recently, we have observed a transition from perturbative to non-perturbative electron dynamics in graphene [1]. The electron dynamics in the non-perturbative regime are well described by the light-field-driven dynamics. In particular, this field-driven dynamics has the same form as repeated Landau-Zener transitions and resultant quantum-path interference around the touching points of graphene's electron bands, known as Landau-Zener-Stückelberg (LZS) interference.

Such Landau-Zener like dynamics are found in various physical systems. Therefore, a comprehensive understanding of this light-field-driven LZS interferometry can provide a general prescription for formulating strong-field dynamics. The purpose of this presentation is to clarify the relations between the parameters involved in this light-field-driven LZS interferometry. For example, we clarify the condition defining the perturbative and the non-perturbative regimes. Relations with strong-field physics in atomic gaseous systems, such as the non-adiabaticity parameter and the intensity parameter, will be discussed.

[1] T. Higuchi, C. Heide, K. Ullmann, H. B. Weber, and P. Hommelhoff, Nature 550, 224 (2017).

MO 1.5 Mon 12:00 K 1.011

**Direct observation of a core-hole spin-orbit wave packet using strong-field spectroscopy** — ●ALEXANDER BLÄTTERMANN, MAXIMILIAN HARTMANN, PAUL BIRK, VEIT STOOSS, GERGANA BORISOVA, CHRISTIAN OTT, and THOMAS PFEIFER — Max-Planck-Institut für Kernphysik, Heidelberg, Deutschland

Spin-orbit coupling and its dynamics play an important role from atomic physics through chemical reactions of molecules up to magnetic properties in material science. Thus far, experimental studies were limited to spin-orbit dynamics in the valence shell of atoms [1]. Here, we present the time-domain observation of ultrafast coherent dynamics among 4d-core-hole states in xenon. The wave packet is created by an extreme-ultraviolet (XUV) light pulse, which lifts a 4d electron to the 6p shell. The natural time-scale of 2.1 fs is dictated by the intrinsically strong fine-structure splitting among the two possible core-hole configurations. Strong-field spectroscopy, i.e., probing the XUV-induced dynamics by means of an intense near-infrared laser pulse [2], allows us to observe these fast wave packet dynamics via a multiphoton-induced coupling of the studied states. These results open a route to site-selective and element-specific studies of coherent electron dynamics in larger systems such as polyatomic molecules and complex solids, where core electrons provide local probes of the electronic structure and dynamics.

[1] Nature 466, 739 (2010)

[2] Science 354, 738 (2016)

MO 1.6 Mon 12:15 K 1.011

**Observation of coherent spin-orbit wave packet dynamics in strong-field generated xenon ions** — ●MAXIMILIAN HARTMANN, ALEXANDER BLÄTTERMANN, PAUL BIRK, VEIT STOOSS, GERGANA BORISOVA, CHRISTIAN OTT, and THOMAS PFEIFER — Max-Planck-Institut für Kernphysik, Heidelberg, Deutschland

Removing the p-shell valence electron of noble gas atoms generates ions, whose ground state forms a doublet due to spin-orbit interaction. As shown theoretically for neon and xenon [1] and experimentally for krypton [2], both ionic state configurations can be populated in a partially coherent way by means of strong-field ionization, which will give rise to coherent dynamics of the thus created wave packet. For the case of xenon, the fine structure splitting reaches 1.3 eV, which leads to dynamics on a time scale of 3 fs.

Here, we present the observation of coherent wave-packet dynamics in field-ionized xenon generated by intense sub-2 cycle laser pulses and probed by means of attosecond transient absorption spectroscopy. Our results constitute a promising step towards understanding the coher-

ent response of multi-electron systems exposed to strong laser fields – especially in the regime of sub-cycle field-induced ionization.

[1] Phys. Rev. A 79, 053402 (2009)

[2] Nature 466, 739 (2010)

## MO 2: Biology Related Molecules

Time: Monday 10:30–12:30

Location: PA 1.150

MO 2.1 Mon 10:30 PA 1.150

**Repelling and Ordering: The Influence of PEG on Protein Adsorption** — ●CHRISTOPH BERNHARD<sup>1</sup>, STEVEN J. ROETERS<sup>2</sup>, JOHANNES FRANZ<sup>1</sup>, TOBIAS WEIDNER<sup>1,2</sup>, MISCHA BONN<sup>1</sup>, and GRAZIA GONELLA<sup>1</sup> — <sup>1</sup>Max Planck Institute for Polymer Research, Mainz, Germany — <sup>2</sup>Aarhus University, Aarhus, Denmark

Nanoparticles and liposomes can be used as versatile drug nanocarriers. Upon injection into the bloodstream a protein layer will immediately coat the nanocarrier surface. This alteration of the surface chemistry can induce changes of the drug carrier properties and interfere with the carrier's targeting mechanism. In order to prevent this non-specific protein adsorption the drug nanocarriers are often coated with a protein repelling PEG layer. However, recently, it has been shown that the adsorption of certain proteins can be beneficial and promote specific cellular uptake. Therefore, a deeper understanding of protein adsorption to PEGylated surfaces is desirable to control the protein corona composition. Here we use mixed lipid monolayers consisting of DMPE and DMPE-PEG2000 as model systems for PEGylated surfaces. We study the influence of interactions between the lipid head groups and the proteins as well as steric repulsion from the PEG chains on the adsorption behavior of bovine serum albumin and fibrinogen. Surface sensitive vibrational sum-frequency generation spectroscopy is used to probe the orientation and structure of the proteins at the lipid/water interface. Our results suggest that an increasing PEG density not only influences the amount of adsorbed proteins, but in the case of Fibrinogen also the ordering at the surface.

MO 2.2 Mon 10:45 PA 1.150

**In-Depth Investigation of the Aggregation Process of Insulin with Time-Resolved Fluorescence Studies** — ●BASTIAN GEISSLER, DIRK WESBERG, and PATRICK NUERNBERGER — Physikalische Chemie II, Ruhr-Universität Bochum, 44780 Bochum

The quaternary structure of proteins can be essential for a certain functionality. On the contrary, misfolded proteins can cause cellular dysfunction and are suspected to determine degenerative diseases like Parkinson's or Alzheimer's disease. Misfolded proteins autocatalytically form insoluble amyloid fibrils, which are commonly known as plaques. The formation of fibrils can be observed with marker dyes like Thioflavin T (ThT) whose fluorescence yield increases during the process due to the modified surrounding. In this study, we employ ThT and measure the aggregation of insulin fibrils using time-resolved fluorescence, either by time-correlated single-photon counting or by a streak camera, and with pulsed excitation alternately at 375 or 405 nm in order to excite different sub-ensembles of the ThT molecules. Whereas the process itself takes hours, we monitor not only the fluorescence yield but also how the lifetimes and emission spectra of ThT change during fibril formation. Since the latter two aspects are associated with the geometry of ThT, we obtain insight into the binding situation of ThT to the fibrils and during the fibril formation.

MO 2.3 Mon 11:00 PA 1.150

**Photorelaxation of Uracil in Explicit Biological Environments** — ●SEBASTIAN REITER, DANIEL KEEFER, and REGINA DE VIVIE-RIEDLE — Department of Chemistry, LMU Munich

Ultraviolet radiation can trigger photochemical reactions in nucleic acids that might result in damage to the genetic code. Such processes are however largely prevented by the intrinsic property of the five canonical nucleobases to dissipate the absorbed energy via ultrafast, non-radiative relaxation pathways. So far, these processes have been investigated mostly on isolated nucleobases in the gas phase. In this context, recent studies elucidate the relaxation process of uracil after optical excitation to the bright S<sub>2</sub> state ( $\pi\pi^*$ ) with femtosecond laser pulses [1, 2]. In our present theoretical work, we go beyond gas phase simulations and investigate uracil in its native RNA environment, where the sugar-phosphate backbone and neighboring nucleobases as well as solvent molecules might influence the relaxation

pathway. For this purpose, we employ an approach that combines wave packet dynamics with molecular dynamics [3] to study the ultrafast population decay from the S<sub>2</sub> excited state through a conical intersection to S<sub>1</sub>, while explicitly taking environmental effects into account. We present our multiscale methodology and discuss the influence of different combinations of neighboring nucleobases and surrounding water molecules on the photostability of uracil.

[1] S. Matsika *et al.*, *J. Phys. Chem. A*, **117**, 12796 (2013).

[2] D. Keefer *et al.*, *J. Am. Chem. Soc.*, **139**, 5061 (2017).

[3] S. Thallmair *et al.*, *J. Chem. Theory Comput.*, **11**, 1987 (2015).

MO 2.4 Mon 11:15 PA 1.150

**Ultrafast Photoinduced Ring Closing in Photoswitchable Diarylethene-Based Nucleosides** — ●JOSE LUIS PEREZ LUSTRES<sup>1</sup>, YANG LI<sup>1</sup>, HANS ROBERT VOLPP<sup>1</sup>, TIAGO BUCKUP<sup>1</sup>, THERESA KOLMAR<sup>2</sup>, ANDRES JAESCHKE<sup>2</sup>, and MARCUS MOTZKUS<sup>1</sup> — <sup>1</sup>PCI, Universität Heidelberg, Germany — <sup>2</sup>IPMB, Universität Heidelberg, Germany

Diarylethene-based nucleosides are novel photoswitchable compounds, where the nucleobase forms the core of the molecular switch.(1) The latter undergoes ring closing/opening reactions upon conrotatory movement of the side chains. The process is reversible and occurs on ultrafast timescales with high yield.(2) Thus, these DNA building blocks are designed to control and report about DNA structure. We address here the ring closing reaction by broadband fs transient absorption in the near UV. The signature of the closed structure is detected in the sub picosecond timescale. Transient anisotropy indicates strong structural reorganisation occurring in the course of vibrational relaxation. Finally, spectral analysis of the non-decaying component demonstrates branching at the earliest stages of the photoreaction. The analysis is facilitated by a novel strategy to isolate the absorption coefficients of the open and closed forms from steady-state UV-Vis absorption spectra obtained during long time irradiation at selected wavelengths.

1. Cahova, H.; Jaeschke, A., *Angew Chem Int Edit* **2013**, *52* (11), 3186-3190.

2. Backup, T.; Sarter, Ch.; Volpp, H.-R.; Jaeschke, A.; Motzkus, M., *J. Phys. Chem. Lett.* **2015**, *6*, 4717-4721.

MO 2.5 Mon 11:30 PA 1.150

**UV-Induced Self-Repair of a DNA Lesion Traced with Quantum Chemistry** — ●DANIEL KEEFER, VITUS BESEL, and REGINA DE VIVIE-RIEDLE — Department of Chemistry, LMU Munich

Nucleobases in DNA and RNA absorb UV light, which can lead to several interesting photophysical and photochemical processes. In a recent experimental study [1], it was revealed that photoexcitation of a guanine (G) adenine (A) sequence can even lead to self-repair of an adjacent cyclobutane pyrimidine dimer (CPD) lesion in oligonucleotides. The proposed mechanism involves photoexcitation of G at 290 nm, followed by a long-living charge transfer state between G and A and subsequent electron donation from the A radical anion to the CPD lesion. This finally induces ring splitting and repair of the damaged nucleobase sequence.

In our theoretical study, we use (multiscale) quantum chemical methods in order to verify this mechanism. The excited states of the GA sequence adjacent to the CPD lesion are computed using high-level active space methods, including explicit consideration of the residual oligonucleotide and the water environment. We will discuss the existence and accessibility of G → A charge transfer states, and trace the time evolution of the experimentally addressed states in the system after photoexcitation by means of semiclassical dynamics.

[1] D. Bucher *et al.* *J. Am. Chem. Soc.* 2016 **138**, 186.

MO 2.6 Mon 11:45 PA 1.150

**Rotational dynamics of indole(H<sub>2</sub>O) dimer clusters** — ●LINDA V. THESING<sup>1</sup>, ANDREY YACHMENEV<sup>1,2</sup>, ROSARIO GONZÁLEZ-FÉREZ<sup>3</sup>, and JOCHEN KÜPPER<sup>1,2,4</sup> — <sup>1</sup>Center for Free-Electron Laser Science,

DESY, Hamburg, Germany — <sup>2</sup>Center for Ultrafast Imaging, Universität Hamburg, Germany — <sup>3</sup>Instituto Carlos I, Universidad de Granada, Spain — <sup>4</sup>Department of Physics, Universität Hamburg, Germany

We present a time-dependent study of the rotational dynamics of a non-rigid molecule in combined ac and dc fields. We compute the alignment and orientation dynamics of the prototypical indole(H<sub>2</sub>O) dimer, including the coupling of the overall rotation to the internal rotation of the water moiety and compare our results to calculations treating the indole(H<sub>2</sub>O) clusters as rigid molecules. We show that due to the small coupling between the rotational and torsional motions, the rigid rotor approximation can be employed for typical field strengths in alignment and orientation experiments. Furthermore, by varying the dependence of the polarizability and electric dipole moment on the torsional angle as well as increasing the external field strengths, we explore regimes where the internal rotation of the water molecule affects the rotational dynamics of the full indole(H<sub>2</sub>O) cluster. We estimate that for laser intensities larger than 10<sup>13</sup> W/cm<sup>2</sup> the influence of the internal rotation of the water molecule can no longer be neglected.

MO 2.7 Mon 12:00 PA 1.150

**Rotationally Resolved Electronic Stark Spectroscopy of 3-Cyanoindole and the 3-Cyanoindole-water Complex** — ●MICHAEL SCHNEIDER, MARIE-LUISE HEBESTREIT, CHRISTIAN HENRICH, and MICHAEL SCHMITT — Institute for Physical Chemistry I, Heinrich-Heine-Universität, Düsseldorf, Germany

The electronic origin of 3-cyanoindole has been investigated using high resolution laser induced fluorescence spectroscopy (HRLIF) to analyze its electronic nature. By means of evolutionary algorithms, molecular parameters like the rotational constants in the electronic ground and first excited state and the orientation of the transition dipole moment were determined. To investigate the permanent dipole moments in the ground and first excited state a homogeneous static electric field was

applied, which lifts the *M* degeneracy by the Stark effect and results in band splittings and shifts.

To understand how solvation influences the electronic nature of the excited state, the binary 3-cyanoindole water cluster was investigated. The different molecular parameters were used to assign the band to optimized CC2-pVTZ structures by comparing the experimental and calculated *ab initio* values.

MO 2.8 Mon 12:15 PA 1.150

**Spatially separated conformers of the dipeptide Ac-Phe-Cys-NH<sub>2</sub>** — ●NICOLE TESCHMIT<sup>1,2,3</sup>, KAROL DŁUGOŁĘCKI<sup>1</sup>, DANIEL GUSA<sup>1</sup>, IGOR RUBINSKY<sup>1</sup>, DANIEL A. HORKE<sup>1,2</sup>, and JOCHEN KÜPPER<sup>1,2,3,4</sup> — <sup>1</sup>Center for Free-Electron Laser Science, DESY, Hamburg, Germany — <sup>2</sup>The Hamburg Center for Ultrafast Imaging, Universität Hamburg, Germany — <sup>3</sup>Department of Chemistry, Universität Hamburg, Germany — <sup>4</sup>Department of Physics, Universität Hamburg, Germany

The conformational separation of biomolecules in the gas phase is an important step toward atomic-resolution diffraction experiments, attosecond dynamics experiments, or kinetic studies of the chemical reactivity of a single conformer.

Here, we present the combination of a laser desorption (LD) source for the vaporization of labile biological molecules [1] with electrostatic control for the spatial separation of conformers [2]. We now demonstrate the conformer separation of the prototypical peptide Ac-Phe-Cys-NH<sub>2</sub>. We detail the characterization and optimization of LD beams, the use of strong field ionization as an universal probe, and the preparation of conformer-pure beams of the Ac-Phe-Cys-NH<sub>2</sub> dipeptide. We analyze options for diffractive imaging of these controlled samples.

[1] N. Teschmit, K. Długołęcki, D. Gusa, I. Rubinsky, D. A. Horke, J. Küpper, *J. Chem. Phys.* 147, 144204 (2017)

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

## MO 3: Photoelectron Spectroscopy

Time: Monday 10:30–12:30

Location: PA 2.150

**Invited Talk** MO 3.1 Mon 10:30 PA 2.150  
**Electronic structure and relaxation of solvated organic molecules studied by time-resolved photoelectron spectroscopy** — JOHAN HUMMERT, GEERT REITSMA, NICOLA MAYER, EVGENII IKONNIKOV, MARTIN ECKSTEIN, and ●OLEG KORNILOV — Max Born Institute, Berlin, Germany

Photoactive processes play a role in many biological systems from human vision to light harvesting. Electronic relaxation and structural rearrangements following photon absorption often strongly depend on the chromophore environment. These dynamics are extensively studied by all-optical techniques, but the tools of time-resolved photoelectron spectroscopy (TRPES), which brought many insights in gas phase and in solid state physics, have not been applied until recently. In this contribution we demonstrate TRPES of organic molecules in aqueous solutions combining monochromatized femtosecond XUV pulses [1] and the microliquid jet technology. We analyze electronic structure of several organic molecules and follow relaxation dynamics of one of them, Quinoline Yellow. Quinoline Yellow in a non-polar aprotic solvent was recently suggested to undergo an excited state proton transfer (ESPT) from a nitrogen to an oxygen atom [2]. Relaxation timescales obtained in our experiment are consistent with this proposal, but the process seems to be faster in water. Additionally, our results indicate an ultrafast solvent rearrangement following a significant change of molecular dipole upon electronic excitation. [1] M. Eckstein et al, *Phys. Rev. Lett.* 116, 163003 (2016) [2] G. R. Han et al, *Sci. Reports*, 7, 3863 (2017)

MO 3.2 Mon 11:00 PA 2.150

**A ps time-resolved photoelectron imaging study on the photophysics of Acenaphthylene** — ●MARCO FLOCK, MAX HERBERT, and INGO FISCHER — Institute of Physical and Theoretical Chemistry, Julius Maximilians University of Würzburg, Germany

Acenaphthylene is a member of the chemical group of polycyclic aromatic hydrocarbons (PAHs). PAHs are a toxic and cancerogen species and are emitted to the environment mainly through incomplete com-

bustion processes. Thus, they are supposed to significantly increase the risk of human cancer diseases. Beside their toxicology, PAHs show interesting photophysical properties and are promising building blocks for devices like semiconductors or solar cells. In our studies, we investigated the excited state dynamics of the S1 and S2 state of Acenaphthylene. Time-resolved TOF photoionization and photoelectron imaging experiments showed an IC transition from the S1 state to the ground state with decreasing lifetimes from 480 ps at the S1 origin to 100 ps at a vibronic excess energy of 2700 cm<sup>-1</sup>. In further experiments, a monoexponential decay after excitation of the S2 state was detected. This can be explained by a very fast IC transition to the high vibronically excited S1 state, followed by another IC to the electronic ground state. The time constant of this second process further decreases to a value of around 55 ps. Besides, time resolved photoelectron images show a constant signal offset at long delay times, which indicates a competing ISC transition to the triplet manifold after S2 excitation.

MO 3.3 Mon 11:15 PA 2.150

**Multi-state Photoelectron Circular Dichroism in Femtosecond Multiphoton Ionization** — ALEXANDER KASTNER<sup>1</sup>, ●TOM RING<sup>1</sup>, ROXANA SAVULEA<sup>1</sup>, BASTIAN C. KRÜGER<sup>2</sup>, G. BARRATT PARK<sup>2</sup>, TIM SCHÄFER<sup>2</sup>, ARNE SENFTLEBEN<sup>1</sup>, and THOMAS BAUMERT<sup>1</sup> — <sup>1</sup>Universität Kassel, Institut für Physik und CINSaT, D-34132 Kassel, Germany — <sup>2</sup>Institut für Physikalische Chemie, Georg-August-Universität Göttingen, D-37077 Göttingen, 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]. Due to the multi-photon ionization, we observed highly structured asymmetries with a magnitude in the range of  $\pm 10\%$  on bicyclic Ketones [3, 4]. By scanning the laser excitation wavelength, up to three electronically distinct resonances can be simultaneously populated. The intermediate state and the excitation wavelength define the photoelectron energy. We report on the depen-

dence of magnitude and sign of PECD on photoelectron energy [5].

- [1] I. Powis, 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)  
 [5] A. Kastner et al., J. Chem. Phys. 147, 013926, (2017)

MO 3.4 Mon 11:30 PA 2.150

**Photoelectron spectroscopy of organic molecules in protic and aprotic solvents** — ●EVGENII IKONNIKOV, JOHAN HUMMERT, GEERT REITSMA, and OLEG KORNILOV — Max Born Institute, Berlin, Germany

The environment of the molecules can cause changes in relaxation dynamics especially in protic solvents, where additional H bonds exist, which cannot be observed in vacuum. Here we use photoelectron spectroscopy in combination with a microliquid jet to study molecules in solution. The method allows us to measure binding energies, energies of excited states and lifetimes using a pump-probe technique. For these experiments we recently developed experimental beamline using HHG [1] to measure time-resolved photoelectron spectra of solvated molecules in water. In this report we present the first results for several solvents and solvated molecules using this technique. Specifically we extend our experiments to protic and non-protic solvents. In time-resolved experiments we use short XUV pulse (30 fs) as a probe pulse and visible 400 nm (30 fs) pulse as a pump-pulse. [1] M. Eckstein et al, Phys. Rev. Lett. 116, 163003 2016

MO 3.5 Mon 11:45 PA 2.150

**Time-resolved photoelectron spectroscopy of deuterated Ethylene in the VUV with interferometric contrast** — ●OLIVER SCHEPP<sup>1</sup>, ARNE BAUMANN<sup>1</sup>, MAREK WIELAND<sup>1,2,3</sup>, and MARKUS DRESCHER<sup>1,2,3</sup> — <sup>1</sup>Institut für Experimentalphysik, Universität Hamburg, Luruper Chaussee 149, 22761 Hamburg — <sup>2</sup>The Hamburg Centre for Ultrafast Imaging (CUI), Luruper Chaussee 149, 22761 Hamburg — <sup>3</sup>Centre for Free-Electron-Laser Science, Universität Hamburg, Luruper Chaussee 149, 22761 Hamburg

Ethylene and its deuterated isotopologues are prototypical molecules for studying non-adiabatic dynamics in small organic systems. Irradiation in the vacuum ultraviolet spectral range gives access to  $\pi \rightarrow \pi^*$  excitation, followed by its ultrafast relaxation to the ground state through two conical intersections, including twisted-pyramidalization and proton migration.

Here we present a scheme using femtosecond vacuum ultraviolet pulses for both pump and probe in a co-propagating geometry enabling interferometric resolution for the pump probe signal [1]. The delay-dependent photoelectron spectra gives access to the ultrafast wavepacket dynamics on different time scales observed for different electron energies. Further, we observe a coherent beating pattern in the pump-probe signal which is attributed to the combined stretch and torsional modes of the C-C double bond.

[1] T. Gebert, D. Rompotis, M. Wieland, F. Karimi, A. Azima, M.

Drescher, New J. Phys. 16 0170347 (2014).

MO 3.6 Mon 12:00 PA 2.150

**Photoelectron Spectroscopy of Triplet Pentadiynylidene and Methylpentadiynylidene** — ●ENGELBERT REUSCH<sup>1</sup>, DOMENIK SCHLEIER<sup>1</sup>, PATRICK HEMBERGER<sup>2</sup>, and INGO FISCHER<sup>1</sup> — <sup>1</sup>Institute of Physical and Theoretical Chemistry, University of Würzburg, Am Hubland, D-97074, Germany — <sup>2</sup>Laboratory for Femtochemistry and Synchrotron Radiation, Paul Scherrer Institut (PSI), CH-5232 Villigen, Switzerland

Highly unsaturated and carbon-rich chain molecules like Pentadiynylidene (HC5H) and Methylpentadiynylidene (MeC5H) occur as unstable intermediates in harsh chemical environments. They are well studied by various techniques like matrix isolated IR, EPR and UV/VIS spectroscopy.[1] Nevertheless, Threshold Photoelectron Spectra (TPES) of HC5H and MeC5H didn't exist. To obtain first insights we applied imaging Photoelectron Photoion Coincidence Spectroscopy in this study, which is capable to supply mass selective TPES. 1-Diazopenta-2,4-diyne and 1-Diazo-hexa-2,4-diyne were selected as excellent precursors generating Triplet Pentadiynylidene and Methylpentadiynylidene. Ensuing the corresponding carbenes were produced by flash pyrolysis, stabilized in the gas phase and photoionized by tunable vacuum ultraviolet synchrotron radiation. This presentation will offer first results in the Photoelectron Spectroscopy of Pentadiynylidene and Methylpentadiynylidene, executed at the Swiss Light Source (SLS) for synchrotron radiation. [1] Bowling, N. P.; Halter, R. J.; Hodges, J. A.; Seburg, R. A.; Thomas, P. S.; Simmons, C. S.; Stanton, J. F.; McMahon, R. J., J. Am. Chem. Soc., 128, 3291-3302 (2006).

MO 3.7 Mon 12:15 PA 2.150

**Energy resolved Auger spectra of thymine after excitation with UV light** — ●JAN METJE<sup>1</sup>, THOMAS J.A. WOLF<sup>2</sup>, and MARKUS GÜHR<sup>1</sup> — <sup>1</sup>University of Potsdam, Potsdam, Germany — <sup>2</sup>Stanford PULSE Institute, SLAC National Accelerator Laboratory, Menlo Park, USA

Energy conversion in UV-excited molecules often involves coupled electronic and nuclear dynamics not fulfilling the Born-Oppenheimer approximation. Their experimental investigation is complicated by the existence of dark  $n\pi^*$  states if the molecule contains heteroatoms. One such chromophore is the model system thymine.

It has been studied with a variety of time-resolved methods including non-resonant Auger and NEXAFS spectroscopy [1,2]. From the former study, it was concluded that the relaxation of UV-excited thymine involves a  $\pi/\pi^* \rightarrow n\pi^*$  transition. The absorption of this  $n\pi^*$  state was observed in integrated Auger spectra of the latter study and determined to happen on a  $(60 \pm 30)$  fs timescale.

We show energy resolved Auger spectra of thymine at resonant absorption lines in NEXAFS spectra after UV excitation and discuss their sensitivity on the molecular relaxation process.

Full author list: see [2] and Jan Metje.

- [1] McFarland et al., Nature Comm. 5:4235, 2014  
 [2] Wolf et al., Nature Comm. 8:29, 2017

## MO 4: Photochemistry

Time: Monday 14:00–15:45

Location: PA 1.150

MO 4.1 Mon 14:00 PA 1.150

**Impact of kilobar Pressures on Ultrafast Photoisomerization Dynamics of a Triazene and of a Thiocyanine System** — ●LENA GRIMMELSMANN<sup>1</sup>, VITOR SCHUABB<sup>2</sup>, BERITAN TEKIN<sup>1</sup>, ROLAND WINTER<sup>2</sup>, and PATRICK NUERNBERGER<sup>1</sup> — <sup>1</sup>Physikalische Chemie II, Ruhr-Universität Bochum, 44780 Bochum — <sup>2</sup>Physikalische Chemie I, Technische Universität Dortmund, 44227 Dortmund

Mechanisms of *cis-trans* photoisomerization can remarkably differ, depending on the actual molecular system and its environment. Previous liquid-phase studies at 1 bar have shown that the triazene compound berenil isomerizes *via* a volume-conserving bicycle-pedal motion, whereas for the thiocyanine NK88 a rotation mechanism with two competing excited-state pathways occurs. For disclosing the associated dynamics, systematic variation of the viscosity of the environment can be highly beneficial. However, if this is done by employing different solvents, the polarity of the solute's surrounding is modified as well to a significant degree. An alternative for adjusting the viscosity is

pressurizing the system, thus keeping polarity changes low. In this study, we apply femtosecond fluorescence upconversion to berenil and NK88 dissolved in 2-propanol or water under pressures of 1 to 1500 bar. For berenil, a negligible impact of the viscosity on the fluorescence dynamics is found, in agreement with the bicycle-pedal motion. By contrast, the two fluorescence lifetimes of NK88 exhibit a prolongation scaling linearly with the viscosity, and their relative amplitudes indicate a pressure-dependent branching ratio for the two accessible photoisomerization pathways.

MO 4.2 Mon 14:15 PA 1.150

**Quantum chemical studies of a hemithioindigo-based photo-driven molecular motor** — ●FLORIAN ROTT<sup>1</sup>, SVEN OESTERLING<sup>1</sup>, LUDWIG HUBER<sup>1</sup>, ROLAND WILCKEN<sup>2</sup>, HENRY DUBE<sup>1</sup>, EBERHARD RIEDLE<sup>2</sup>, and REGINA DE VIVIE-RIEDLE<sup>1</sup> — <sup>1</sup>Department of Chemistry, LMU Munich — <sup>2</sup>Lehrstuhl für BioMolekulare Optik, LMU Munich

In recent years photodriven molecular motors drew increasing interest

due to their ability to convert light energy into directional motion. A hemithioindigo-based photodriven molecular motor was recently synthesized by Dube and Coworkers [1]. This motor performs a full 360° rotation after excitation with visible light, showing unidirectionality at a very fast rate of potentially up to 1 KHz at 20°C. The full rotation is believed to be a four step process consisting of two light induced and two thermal steps. However until now, the mechanism accounting for this fast rotation is not completely understood. We present possible pathways for the light-induced steps based on excited state quantum chemical calculations at the CASSCF level of theory. The calculations are compared to newly available results from time-resolved pump-probe experiments.

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

MO 4.3 Mon 14:30 PA 1.150

**Ultrafast Photoinduced dynamics of Benzocyclobutenedione in Solution** — ●XIAONAN MA, HANS-CHRISTIAN SCHMITT, MICHAEL WENZEL, MARCO FLOCK, INGO FISCHER, ROLAND MITRIĆ, and TOBIAS BRIXNER — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

Benzocyclobutenedione (BCBD) has an abundant photochemistry and has been studied since decades, but its sub-ns photochemical dynamics remained unknown. In this work, the ultrafast photophysics and photochemistry of BCBD dissolved in dichloromethane was investigated by transient IR and UV/Vis absorption spectroscopy. The initial UV-populated  $S_3(\pi\pi^*)$  state deactivates rapidly to the  $S_1(n\pi^*)$  state via internal conversion (IC) followed by sub-ps vibrational relaxation (VR). In parallel, the  $S_1(v > 0)$  state BCBD decarbonylates to benzocyclopropenone, which subsequently rearranges to cyclopentadienyldieneketene. Two extra reactions on the  $S_1(v = 0)$  state that compete with deactivation to  $S_0$  were identified by transient IR spectra combined with DFT/TDDFT calculations. Ring-opening in the  $S_1(v = 0)$  state produces vibrationally hot bicyclic cools within 22 ps. This process competes with the intramolecular rearrangement to singlet oxacarbene and subsequent conversion into the triplet carbene via intersystem crossing (ISC). A long time product identified in the transient UV/Vis spectra is probably due to dimerization of the carbene. Molecular dynamics (MD) simulations of the early-time photochemistry of BCBD successfully reproduce the formation of benzocyclopropenone and oxacarbene.

MO 4.4 Mon 14:45 PA 1.150

**Fluorescence studies on photosensitizers based on thermally activated delayed fluorescence (TADF) dyes** — ●AYLA PÄPCKE<sup>1</sup>, HENRIK JUNGE<sup>2</sup>, STEFAN LOCHBRUNNER<sup>1</sup>, MATTHIAS BELLER<sup>2</sup>, and SHU-PING LUO<sup>3</sup> — <sup>1</sup>Institut für Physik, Universität Rostock, Albert-Einstein-Straße 23, 18059 Rostock — <sup>2</sup>Leibniz-Institut für Katalyse an der Universität Rostock e.V. — <sup>3</sup>State Key Laboratory Breeding Base of Green Chemistry-Synthesis Technology, Zhejiang University of Technology

As a result of the increasing scarcity of fossil fuels renewable energy fuels generated with the help of solar energy become a focus in current research. Photosensitizers responsible for the absorption of sun light play here a key role. In water reduction systems thermally activated delayed fluorescence (TADF) dyes can be used as efficient organic sensitizers. After an absorption event the water reduction catalyst (WRC) has to remove an electron from the excited singlet state of the TADF dye. The WRC acts as a mediator transferring the electron to protons in the water generating free hydrogen in a final step. Applying time resolved and stationary fluorescence measurements to the TADF dyes in the presence and absence of the WRC we investigate, if the proposed reaction scheme is indeed operational, and characterize the efficiency of the photo induced electron transfer steps.

MO 4.5 Mon 15:00 PA 1.150

**The Femtochemistry of the Ferrioxalate Actinometer** — ●STEFFEN STRAUB, JÖRG LINDNER, and PETER VÖHRINGER — Institut für Physikalische und Theoretische Chemie, Universität Bonn,

Wegelerstrasse 12, 53177 Bonn, Germany

The ferrioxalate actinometer is an aqueous solution of the complex anion, potassium trisoxalatoferriate(III), which is frequently used in preparative photochemistry to determine the internal radiant flux of photoreactors. Actinometers are needed to quantify the quantum yield and hence, the total efficiency of a photochemical reaction of interest. In the presence of light, ferrioxalate is reduced to ferrous oxalate and a neutral carbon dioxide together with a free oxalate anion is released from the complex. Despite having served as the "gold Standard" of liquid-phase actinometry for many years, the primary processes of ferrioxalate are entirely unknown. Previous femtosecond (fs) UV-pump/Vis-probe experiments and most recent ultrafast x-ray absorption spectroscopy have yielded ambiguous and partly contradictory results. Here, we report on fs-UV-pump mid-infrared probe spectroscopy, which is able to provide unique structural-dynamical information about the complex following its initial ultrafast optical excitation. The fs-spectra demonstrate that a hot CO<sub>2</sub> molecule is expelled from coordination sphere of the ferric center within 500 fs to generate a penta-coordinated ferrous species that bears an intriguing carbon dioxide radical anion ligand. A subsequent structural isomerization on a 10 ps-time scale and the loss of the CO<sub>2</sub> moiety yields the final ferrous product of the actinometer.

MO 4.6 Mon 15:15 PA 1.150

**Time-Resolved step-scan FTIR investigation of transition metal containing complexes** — ●PATRICK DI MARTINO-FUMO<sup>1</sup>, MANUEL ZIMMER<sup>1</sup>, SVEN OTTO<sup>2</sup>, HANNA WAGNER<sup>3</sup>, FRANK BREHER<sup>3</sup>, WIM KLOPPER<sup>4</sup>, KATJA HEINZE<sup>2</sup>, and MARKUS GERHARDS<sup>1</sup> — <sup>1</sup>Physical Chemistry, TU Kaiserslautern, Germany — <sup>2</sup>Inorganic Chemistry and Analytical Chemistry, Johannes Gutenberg University, Germany — <sup>3</sup>Inorganic Chemistry, KIT, Germany — <sup>4</sup>Physical and Theoretical Chemistry, KIT, Germany

In this contribution, the time-resolved step-scan FTIR technique is used for investigations of transition metal-complexes in their electronically excited states with lifetimes in the microsecond regime. The vibrational frequencies obtained from this technique compared with theoretical predictions allow a structural assignment of the excited states. In addition, the influence of temperature can be investigated due the possibility to cool down a solid sample to at least 20 K, which e.g. results in an increase of lifetimes and an exclusive population of the lowest excited state. The chosen molecular systems include a mononuclear Cr<sup>3+</sup>-complex with dipyrindinium ligands. This complex has a very high luminescence quantum yield and two energetically similar doublet states. Additionally, investigations on a catalytically active multinuclear complex with two ruthenium and three copper ions including tris(3-pyridin-2-yl)pyrazole ligands is presented. By comparison of calculated (DFT) and experimental spectra a significant geometry change between the electronic ground state (singlet) and the excited triplet state can be identified.

MO 4.7 Mon 15:30 PA 1.150

**Spectroscopic Investigation of Fe(II)-Complexes on the fs-Time Scale** — ●ALEKSEJ FRIEDRICH<sup>1</sup>, PETER ZIMMER<sup>2</sup>, MATTHIAS BAUER<sup>2</sup>, and STEFAN LOCHBRUNNER<sup>1</sup> — <sup>1</sup>Institute of Physics, University of Rostock — <sup>2</sup>Department Chemie, Universität Paderborn

Iron-complexes are interesting for photocatalytic applications, because they could act as photosensitizers and replace noble metals. A problem of such Fe-complexes is a short lifetime of the metal-to-ligand charge transfer state (MLCT). One promising way to extend the lifetime is to use ligands in the complex with N-heterocyclic carbene (NHC) moieties.

To get insight into the impact of the NHC ligands on the photophysics of the complexes ultrafast transient absorption measurements are performed. We see a nice correlation between the number of NHC sites and the lifetime of the MLCT state. Fe(II)-complexes with a low NHC number (2) relax from the MLCT state to the lowest metal-centered state within 100 fs while four NHC sites result in a MLCT lifetime of 8 ps.[1]

[1] P. Zimmer et al., *Inorg. Chem.*, accepted.



## MO 5: X-Ray and XUV Spectroscopy (joint session MO/A)

Time: Monday 14:00–15:45

Location: PA 2.150

## Invited Talk

MO 5.1 Mon 14:00 PA 2.150

**Theoretical soft X-ray spectroscopy of transition metal compounds: A multi-reference wave function approach** — ●SERGEY I. BOKAREV — Institut für Physik, Universität Rostock, Albert-Einstein-Str. 23-24, 18059, Rostock

To date, X-ray spectroscopy has become a routine tool that can reveal highly local and element-specific information on the electronic structure of atoms in complex environments. Here, we aim at the development of an efficient and versatile theoretical methodology for the treatment of soft X-ray spectra of transition metal compounds mainly based on the multi-configurational self-consistent field electronic structure theory combined with a perturbative LS-coupling scheme for spin-orbit coupling. A special focus is put on the L-edge photon-in/photon-out and photon-in/electron-out processes, i.e. X-ray absorption, resonant inelastic scattering, partial fluorescence yield, photoelectron and Auger spectroscopy treated on the same theoretical footing. We address the application of the X-ray metal L-edge and ligand K-edge as well as XUV spectroscopy to unraveling electronic structure and nature of chemical bonds, oxidation and spin-states, the interplay of radiative and non-radiative decay channels, fingerprints of nuclear dynamics and non-adiabatic transitions as well as ultrafast electron dynamics triggered by X-ray light. The investigated systems range from the small prototypical coordination compounds and catalysts to the aggregates of biomolecules.

MO 5.2 Mon 14:30 PA 2.150

**Solving the Graphene Oxide Puzzle - a TDDFT-XAS Study** — ●FABIAN WEBER, JIAN REN, TRISTAN PETIT, and ANNIKA BANDE — Helmholtz-Zentrum Berlin

Graphene Oxide (GO) quantum dots and its derivatives have proven to be a resource efficient material for photocatalytic water splitting. Due to the amorphous nature of GO derived materials, it has however not been possible yet to fully understand what structural features are allowing the catalytic reaction.

Since X-Ray spectroscopy is a standard technique to identify neighbouring functionalities in a very selective way, we developed a time-dependent density functional theory (TDDFT) approach to probe the constitution of single specific atoms in model systems in a meaningful way. Since these localized Carbon K-edge XAS-spectra have shown to be specific up to about 3 chemical bonds, we may use a multitude of model systems of relatively small size to generate a surrounding-specific database of several unique functionalization patterns.

In this talk we show how systematic comparison of this database of several hundreds of different surrounding-specific XAS spectra with experimental data leads to a straightforward method to gain insights on structural features of amorphous materials.

MO 5.3 Mon 14:45 PA 2.150

**Hydrogen bond dissociation dynamics of indole-water clusters** — ●MELBY JOHNY<sup>1</sup>, THOMAS KIERSPEL<sup>1,2</sup>, JOSS WIESE<sup>1,2</sup>, JOLIJN ONVLEE<sup>1</sup>, HELEN BIEKER<sup>1,2</sup>, TERRY MULLINS<sup>1,2</sup>, ANDREA TRABATTONI<sup>1</sup>, RUTH LIVINGSTONE<sup>1,2</sup>, SEBASTIAN TRIPPEL<sup>1,2</sup>, JOCHEN KÜPPER<sup>1,2,3</sup>, and AND OTHERS<sup>1,2,3</sup> — <sup>1</sup>Center for Free Electron Laser Science (CFEL), Deutsches Elektronen Synchrotron (DESY), Hamburg, Germany — <sup>2</sup>The Hamburg Center for Ultrafast Imaging, University of Hamburg, Germany — <sup>3</sup>Department of Physics, University of Hamburg, Germany

The properties of atoms and molecules are strongly dependent on their local environment and hydrogen bonds are of universal importance in chemistry and biochemistry. Therefore, it is highly desirable to bridge the gap between single, isolated molecules and molecules in solvation. Photophysics of microsolvated indole is significantly relevant being strongest UV chromophore of tryptohan as well as the structure of singly hydrogen bonded indole-water cluster is known [1].

Here, we show our recent experiment performed at LCLS at SLAC for the investigation of hydrogen bond breaking dynamics of indole-water clusters via UV-pump (266 nm) and x-ray probe (2.5 nm) photoelectron-photoion-photoion-coincidence (PEPIPICO) imaging. Our preliminary analysis shows time-dependent dissociation channels with distinguishable velocities for hydronium ions detected in coincidence with the photo-fragments of indole.

[1] Korter, Pratt, Küpper, J. Phys. Chem. A 1998, 102, 7211-7216

MO 5.4 Mon 15:00 PA 2.150

**Time-Resolved Pump-Probe Spectroscopy of XUV-induced Dynamics in Water, Ammonia and Methanol Clusters** — ●RUPERT MICHIELS<sup>1</sup>, AARON LAForge<sup>1</sup>, MATTHIAS BOHLEN<sup>1</sup>, CARLO CALLEGARI<sup>2</sup>, ANDREW CLARK<sup>3</sup>, MARCEL DRABELLS<sup>3</sup>, KEVIN C. PRINCE<sup>2</sup>, STEFANO STRANGES<sup>4</sup>, MARCELLO CORENO<sup>5</sup>, OKSANA PLEKAN<sup>2</sup>, VERONICA OLIVER<sup>3</sup>, AARON VON CONTA<sup>6</sup>, MARTIN HUPPERT<sup>6</sup>, HANS-JAKOB WÖRNER<sup>6</sup>, and FRANK STIENKEMEIER<sup>1</sup> — <sup>1</sup>Universität Freiburg, Germany — <sup>2</sup>Elettra-Sincrotrone Trieste, Italy — <sup>3</sup>Ecole Polytechnique Fédérale de Lausanne, Switzerland — <sup>4</sup>University Sapienza, Italy — <sup>5</sup>ISM-CNR, Trieste, Italy — <sup>6</sup>ETH Zürich, Switzerland

Results for ammonia, methanol and water clusters investigating the dynamics upon XUV ionization with the FERMI free electron laser are presented. In an XUV-UV pump-probe scheme we obtain a time-resolved picture of the resulting fragments and their electronic states. Recombination and molecular dissociation lead to a great variety of electron energies and ionic fragments that give insight into the underlying dynamics. The vertical detachment energies of the electrons and masses of the ions were measured by means of a VMI velocity map imaging detector combined with a time-of-flight mass spectrometer which also allows a covariance analysis.

## Invited Talk

MO 5.5 Mon 15:15 PA 2.150

**Tracing the spatial and electronic structure of excited molecules using X-ray FEL and HHG light** — ●KIRSTEN SCHNORR — Max-Planck-Institut für Kernphysik — University of California Berkeley

Free-Electron Lasers (FELs) are capable of producing intense and ultrashort X-ray pulses, which enable femtosecond time-resolved diffractive imaging experiments. This allows to initiate chemical reactions in molecules using an optical pump pulse and probing the induced changes in the nuclear structure by X-ray scattering using a delayed FEL pulse. Here, results on the strong-field induced dynamics of C<sub>60</sub> molecules probed by soft and hard X-ray scattering will be presented.

A soft X-ray source based on high harmonic generation with photon energies up to 310 eV has been successfully commissioned and first time-resolved experiments carried out. Transient absorption experiments on the UV-induced dynamics of small carbon containing molecules, probed with a broadband soft X-ray pulse, will be shown.

## MO 6: Atomic Clusters I (joint session A/MO)

Time: Monday 16:15–17:45

Location: K 2.016

## Invited Talk

MO 6.1 Mon 16:15 K 2.016

**Halo states in helium dimers/trimers** — ●REINHARD DOERNER<sup>1</sup>, MAKSIM KUNITSKI<sup>1</sup>, STEFAN ZELLER<sup>1</sup>, LOTHAR SCHMIDT<sup>1</sup>, TILL JAHNKE<sup>1</sup>, MARKUS SCHÖFFLER<sup>1</sup>, DÖRTE BLUME<sup>2</sup>, JÖRG VOITSBERGER<sup>1</sup>, FLORIAN TRINTER<sup>1</sup>, and ANTON KALININ<sup>1</sup> — <sup>1</sup>Goethe Universität Frankfurt Germany — <sup>2</sup>Washington State University USA

We will show experimental imaging the Helium dimer, trimer and the

Efimov state of He<sub>3</sub>. We will also show movies of the rotational response of halo states to a nonresonant short laser pulse.

MO 6.2 Mon 16:45 K 2.016

**Rotating rotationless: nonadiabatic alignment of the helium dimer** — ●MAKSIM KUNITSKI<sup>1</sup>, QINGZE GUAN<sup>2</sup>, STEFAN ZELLER<sup>1</sup>, DÖRTE BLUME<sup>2</sup>, and REINHARD DÖRNER<sup>1</sup> — <sup>1</sup>Institut für Kernphysik, Goethe-Universität Frankfurt am Main — <sup>2</sup>Department of

Physics and Astronomy, University of Oklahoma

Quantum mechanically rotational and vibrational dynamics in molecules is time evolution of corresponding wave packets. Such dynamics can be periodic, as well-known rotational and vibrational revivals with wave packets consisting of many coherently prepared bound states. How the rotational and vibrational dynamics would look like in a molecular system with a single bound state? One of such extreme quantum system is the helium dimer, where the two-body potential supports only one state.

We applied the nonadiabatic "kick" to the helium dimer by a femtosecond laser pulse (pump) and watched evolution of the system by Coulomb explosion imaging, which was initiated by the second much more intense delayed probe pulse. The observed time-dependent alignment of the helium dimer, as well as time evolution of the rovibronic wave packet, is going to be discussed.

MO 6.3 Mon 17:00 K 2.016

**Evidence of angulon quasiparticles formation in superfluid  $^4\text{He}$  nanodroplets** — ●IGOR CHEREPANOV, GIACOMO BIGHIN, and MIKHAIL LEMESHKO — IST Austria (Institute of Science and Technology Austria), Am Campus 1, 3400, Klosterneuburg, Austria

Quasiparticles are a core concept in many-body physics widely used for solving quantum impurity problems [1]. Models based on quasiparticles serve as an alternative to theories implying extensive numerical calculations. Moreover, they provide a more straightforward and intuitive understanding of complex phenomena taking place in many-body systems. Here we present the evidence for the formation of angulon quasiparticles [2] in experiments on trapping molecules in superfluid  $^4\text{He}$  nanodroplets. The angulon consists of a rotating impurity (such as a molecule) dressed by a field of surrounding bath excitations (phonons, rotons etc.). Anisotropic interactions of the impurity with helium give rise to a number of many-body effects, such as angulon instabilities – resonant transfer of a small amount of angular momentum from the molecule to the superfluid. We demonstrate that broadening and splitting of spectral lines as well as a violation of rotational selection rules can be explained by means of angulon instabilities [3]. Furthermore, the dynamical emergence of angulon instabilities affects the time evolution of a rotational wavepacket and therefore may be detected in experiments on impulsive molecular alignment in  $^4\text{He}$  droplets.

[1] M. Lemeshko, Phys. Rev. Lett. **118**, 095301 (2017)

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

[3] I. Cherepanov, M. Lemeshko, Phys. Rev. Materials **1**, 035602 (2017)

MO 6.4 Mon 17:15 K 2.016

**Decoherence in the dissociation of the alkali-helium droplet system** — ●MARCEL BINZ, LUKAS BRUDER, ULRICH BANGERT, DANIEL UHL, and FRANK STIENKEMEIER — Institute of Physics, University of Freiburg, Germany

The intriguing properties of the alkali (Ak)-helium droplet system have been extensively studied in the past by several groups. The broadened Ak absorption lines were successfully explained by a pseudo-diatom molecule model, and the dissociation of this pseudo molecular system was studied in detail with fs pump probe experiments. As an intriguing aspect of the dissociation, we have in a recent study investigated the temporal evolution of an electronic coherence induced in the parent system and follow this evolution in the desorbing Ak atom. For this purpose, we have applied coherent nonlinear spectroscopy to our helium droplet machine. Our scheme is particularly sensitive to the time evolution of coherences and allows us to follow the dissociation with high spectro-temporal resolution.

MO 6.5 Mon 17:30 K 2.016

**Resonante Ionisation dotierter Heliumtropfen** — ●MICHAEL KELBG<sup>1</sup>, LEV KAZAK<sup>1</sup>, MICHAEL ZABEL<sup>1</sup>, ANDREAS HEIDENREICH<sup>2</sup>, JOSEF TIGGESBÄUMKER<sup>1</sup> und KARL-HEINZ MEIWES-BROER<sup>1</sup> — <sup>1</sup>Universität Rostock, Inst. f. Physik, Rostock, Germany — <sup>2</sup>Ikerbasque, Basque Foundation for Science, Bilbao, Spain

Heliumtropfen sind für NIR-Laserpulse transparent und können erst bei hohen Intensitäten durch Feldionisation ionisiert werden. Durch eine Dotierung des Tropfens mit Metallen oder anderen Edelgasen als Ionisationskeim ist es jedoch bereits für deutlich niedrigere Intensitäten möglich den gesamten Heliumtropfen lawinenartig zu ionisieren. Besonders effektiv wird dieser Prozess durch Anregung mittels zwei getrennter Pulse, wobei der erste Puls ein Plasma erzeugt, und der zweite Puls dann durch Erreichen der Bedingungen für die Mie-Resonanz einen optimalen Energietransfer ermöglicht.

Eine Dotierung mit Xenon führt zu einem leicht zu ionisierendem Cluster im Zentrum des Heliumtropfens. Die Effektivität einer resonanten Anregung äußert sich hier durch die Erzeugung von sehr hohen Ladungszuständen des Xenons bis zu Xe<sup>23+</sup>. Ein völlig anderes Bild zeigt sich bei Dotierung mit Magnesium. Dieses bildet zunächst einen sogenannten Magnesiumschaum, bei dem die einzelnen Magnesiumatome im Abstand von 10 Å voneinander in einem metastabilen Zustand verharren. Durch Anregung des Magnesiums unterhalb der Ionisationsenergie lässt sich ein Kollaps des Magnesiumschaums induzieren.

Zuletzt wird die Elektronenemission aus dem Tropfen bei unterschiedlicher Dotierung und Anregung untersucht.

## MO 7: High Resolution Spectroscopy

Time: Monday 16:15–17:45

Location: PA 1.150

MO 7.1 Mon 16:15 PA 1.150

**Dipole Moments of Anisole in Ground and Excited State via Condensed Phase Thermochromic Spectroscopy and Gas Phase HRLIF Spectroscopy** — ●MIRKO LINDIC, MICHAEL SCHNEIDER, MARIE-LUISE HEBESTREIT, and MICHAEL SCHMITT — Institute for Physical Chemistry I, Heinrich-Heine-University, Düsseldorf

The dipole moment of anisole in ground and first excited singlet states was investigated and compared for the gas and the condensed phase. The dipole moments in solution have been determined using the method of thermochromic shifts of the fluorescence emission and absorption spectra. To test the validity of the method the simple model molecule anisole was measured with temperature dependent UV/Vis-absorption and fluorescence spectroscopy. Contrary to previous studies, the solvent cavity volume was determined experimentally via concentration dependent density measurements. To create exact values for comparison with those from the condensed phase high resolution laser induced fluorescence Stark spectra have been measured in order to reliably determine the excited state dipole moments for a direct comparison. A critical survey about the method will be given.

MO 7.2 Mon 16:30 PA 1.150

**High-Resolution CARS Spectroscopy of the  $\text{T}_2$  molecule** — ●MAGNUS SCHLÖSSER<sup>1</sup>, XIAODONG ZHAO<sup>1</sup>, MADHU TRIVIKRAM<sup>2</sup>, WIM UBACHS<sup>2</sup>, and EDCEL J. SALUMBIDES<sup>2</sup> — <sup>1</sup>Tritium Laboratory Karlsruhe, Karlsruhe Institute of Technology, Eggenstein-

Leopoldshafen, Germany — <sup>2</sup>LaserLaB and Department of Physics and Astronomy, Vrije Universiteit, Amsterdam, The Netherlands

Molecular hydrogen is a benchmark system for bound state quantum calculation and tests of quantum electrodynamical effects. While spectroscopic measurements on the stable species have progressively improved over the years, high-resolution studies on the radioactive isotopologues  $\text{T}_2$ , HT and DT have been limited. For this reason, we have built a high-resolution coherent anti-Stokes Raman spectroscopy system using nano-second pulses at the LaserLab Amsterdam and equipped it with a specially designed gas cell filled with  $< 1\text{GBq}$  of  $\text{T}_2$  from the Tritium Laboratory Karlsruhe. Here, we present an accurate determination of  $\text{T}_2$  ( $Q(J = 0 \dots 5)$ ) transition energies in the fundamental vibrational band of the ground electronic state, with the present experimental uncertainty of  $0.02\text{cm}^{-1}$ , which is a fivefold improvement over previous measurements, agreement with the latest theoretical calculations is demonstrated.

MO 7.3 Mon 16:45 PA 1.150

**Precision Spectroscopy of the Hydroxyl Radical** — ●ARTHUR FAST<sup>1</sup>, JOHN E. FURNEAUX<sup>2</sup>, and SAMUEL A. MEEK<sup>1</sup> — <sup>1</sup>Max Planck Institute for Biophysical Chemistry, Germany — <sup>2</sup>University of Oklahoma, USA

We present results on optical frequency comb referenced spectroscopy of the  $\text{A } ^2\Sigma^+, v' = 0 \leftarrow \text{X } ^2\Pi_{3/2}, v'' = 0, J'' = \frac{1}{2}$  transitions in OH. The comb spans from 1064 nm to 532 nm and is locked to a Nd:YAG

laser. This laser is, in turn, stabilized to a molecular iodine transition using saturated absorption spectroscopy, resulting in a relative short-term stability of better than  $10^{-12}$ . The A-X transitions near 308 nm are measured using laser-induced fluorescence in a supersonic molecular beam. The spectroscopy laser is a frequency-doubled CW dye laser which is directly stabilized to the comb. A sub 100 kHz measurement precision allows us to determine the spectroscopic constants much more precisely, up to two orders of magnitude better than the current literature values.

MO 7.4 Mon 17:00 PA 1.150

**Observation of 1,2-, 1,3- and 1,4-dimethoxybenzenes via high resolution laser induced fluorescence Stark spectroscopy** — •MARIE-LUISE HEBESTREIT, MICHAEL SCHNEIDER, CHRISTIAN HENRICH, and MICHAEL SCHMITT — Institute for Physical Chemistry I, Heinrich-Heine-University, Düsseldorf

The different rotamers of 1,2-, 1,3- and 1,4-dimethoxybenzene were investigated using high resolution laser induced fluorescence spectroscopy. The molecular parameters, obtained from fit using a evolutionary strategies were compared to the results of *ab initio* calculations and used for structural assignment. To investigate the permanent dipole moments moments in the ground and first electronically excited singlet state, a homogeneous field was applied, which lifts the *M* degeneracy by the Stark effect. The resulting experimental permanent dipole moments were compared to predicted dipole moments via vectorial addition of the anisole dipoles and to the results of *ab initio* calculations.

Finally, the conformational space of 1,3-dimethoxybenzene is discussed in particular.

MO 7.5 Mon 17:15 PA 1.150

**Probing a possible variation of the proton-to-electron mass ratio in the hyperfine-structure of ammonia, a theoretical study** — •ANDREI DUCHKO<sup>1,4</sup>, ALEC OWENS<sup>1,2</sup>, ANDREY YACHMENEV<sup>1,2</sup>, and JOCHEN KÜPPER<sup>1,2,3,4</sup> — <sup>1</sup>Center for Free-Electron Laser Science, DESY, Hamburg, Germany — <sup>2</sup>Center for Ultrafast Imaging, Universität Hamburg, Germany — <sup>3</sup>Department of Physics, Universität Hamburg, Germany — <sup>4</sup>Department of Chemistry, Universität Hamburg, Germany

In this study we investigate a possible variation of the proton-to-

electron mass ratio ( $\mu$ ) in the hyperfine transitions of the rovibrational spectrum of ammonia. The rovibrational spectrum has been computed variationally using the program suite TROVE [1,2], a new spectroscopically determined potential energy surface [3], and *ab initio* quadrupole [2], spin-spin, and spin-rotation coupling surfaces. The computed spectrum covers transitions between levels with rotational excitations up to  $J = 15$  and vibrational band centers up to  $8000 \text{ cm}^{-1}$  above the zero point energy. Comparison with experimental data confirms the high accuracy of the computed results, which is essential for modeling the hyperfine-resolved high-resolution spectra. We will present an extensive analysis of the  $\mu$ -variation sensitivity coefficients of hyperfine transitions of ammonia in the microwave and infrared spectral regions.

[1] Yurchenko S. N., Thiel W., Jensen P., 2007, *J. Mol. Spectrosc.*, 245, 126. [2] Yachmenev A., Küpper J., 2017, *J. Chem. Phys.*, 147, 141101. [3] Coles, P., Yurchenko, S. N., Tennyson, J., 2017, in preparation

MO 7.6 Mon 17:30 PA 1.150

**The role of dispersion in the structure of diphenyl ether aggregates** — •FABIAN DIETRICH<sup>1</sup>, DOMINIC BERNHARD<sup>1</sup>, MARIYAM FATIMA<sup>2</sup>, ANJA POBLOTZKI<sup>3</sup>, MARTIN SUHM<sup>3</sup>, MELANIE SCHNELL<sup>2</sup>, and MARKUS GERHARDS<sup>1</sup> — <sup>1</sup>Physical Chemistry and Research Center Optimas, TU Kaiserslautern, Germany — <sup>2</sup>DESY Hamburg, Germany — <sup>3</sup>Physical Chemistry, University Göttingen, Germany

Dispersion interactions can play an important role to understand unusual binding behaviors. This is illustrated here by a systematic study on the structural preferences of diphenyl ether (DPE)-alcohol aggregates, for which either an OH-O or an OH- $\pi$  bound isomer can be formed. The alcohol molecules range from methanol to adamantanol. Investigations of the DPE-water complex complete this series. The experimental investigations are performed by IR/UV-methods, microwave spectroscopy, and FTIR spectroscopy, tightly connected with a detailed theoretical analysis. The resulting solvent-size-dependent trend on the structural preference turns out to be counter-intuitive, i.e., the hydrogen-bonded OH-O structures become more stable for larger alcohols, which are expected to be stronger dispersion energy donors and thus should prefer an OH- $\pi$  arrangement. Quantification of dispersion interactions in combination with the twisting of the ether upon solvent aggregation are found to be a key for understanding this preference.

## MO 8: Ultrafast Spectroscopy with XUV (joint session MO/A)

Time: Monday 16:15–17:45

Location: PA 2.150

### Invited Talk

MO 8.1 Mon 16:15 PA 2.150

**Measurement of femtosecond dynamics in HCL molecules with THz streaking** — KATHARINA WENIG<sup>1</sup>, MAREK WIELAND<sup>1</sup>, SOPHIE WALTHER<sup>1</sup>, ARNE BAUMANN<sup>1</sup>, ANASTASIOS DIMITRIOU<sup>1</sup>, MARK PRANDOLINI<sup>1</sup>, OLIVER SCHEPP<sup>1</sup>, IVETTE BERMUNDEZ MACHIAS<sup>2</sup>, MALTE SUMFLETH<sup>1</sup>, NIKOLA STOJANOVIC<sup>2</sup>, STEFAN DÜSTERER<sup>2</sup>, JULIANE RÖNTSCH-SCHULENBURG<sup>2</sup>, MARKUS DRESCHER<sup>1</sup>, and •ULRIKE FRÜHLING<sup>1</sup> — <sup>1</sup>Institut für Experimentalphysik, Universität Hamburg, Deutschland — <sup>2</sup>Deutsches Elektronen-Synchrotron DESY, Hamburg, Deutschland

We have studied the ultrafast electronic decay of core excited HCL molecules directly in the time domain. In the experiment we used femtosecond XUV pulses from the free-electron laser in Hamburg (FLASH) to resonantly excite  $2p_{3/2}$  core electrons to the antibonding  $\sigma^*$  orbital. After the excitation the molecules dissociate and the electronic excitation relaxes via the emission of an Auger-electron. In order to follow the evolution of this coupled electronic and nuclear dynamics we have collinearly superimposed the exciting XUV pulses with intense THz pulses from the FLASH THz undulator. Electrons emitted from the molecules are accelerated (streaked) by the THz electric field whereby the resulting momentum change depends on the THz phase at the ionization time. Thus the ionization dynamics can be studied by measuring the streaked electron spectra. In the talk the experimental technique and first experimental results will be presented.

MO 8.2 Mon 16:45 PA 2.150

**A chemical understanding of the lack of site-specificity in molecular inner-shell photofragmentation** — •LUDGER INHETER<sup>1,2</sup>, BART OOSTENRIJK<sup>3</sup>, SANG-KIL SON<sup>1,2</sup>, ROBIN

SANTRA<sup>1,2,4</sup>, LINDA YOUNG<sup>5</sup>, and STACEY L. SORESENSEN<sup>3</sup> — <sup>1</sup>Center for Free-Electron Laser Science, DESY — <sup>2</sup>The Hamburg Centre for Ultrafast Imaging — <sup>3</sup>Department of Physics, Lund University — <sup>4</sup>Department of Physics, University of Hamburg — <sup>5</sup>Argonne National Laboratory

In many cases fragmentation of molecules upon inner-shell ionization is very unspecific with respect to the initially localized ionization site. Often this finding is interpreted in terms of an equilibration of internal energy into vibrational degrees of freedom after Auger decay. Here we investigate the x-ray photofragmentation of ethyl trifluoroacetate upon core electron ionization at environmentally distinct carbon sites using photoelectron-photoion-photoion coincidence measurements and *ab-initio* electronic structure calculations. For all the 4 carbon ionization sites, the Auger decay weakens the same bonds and transfers the two charges to opposite ends of the molecule, which leads to a rapid dissociation into 3 fragments followed by further fragmentation steps. The lack of site-specificity is attributed to the character of the dicationic electronic states after Auger decay, instead of a fast equilibration of internal energy.

MO 8.3 Mon 17:00 PA 2.150

**Electron-ion coincidence spectroscopy on small quantum systems** — •LENA WORBS<sup>1</sup>, ANDREAS PRZYSTAWIK<sup>1</sup>, DAVID SCHWICKERT<sup>1</sup>, SERGEY USENKO<sup>1,2</sup>, and TIM LAARMANN<sup>1,2</sup> — <sup>1</sup>Deutsches Elektronen-Synchrotron DESY, Notkestrasse 85, Hamburg 22607, Germany — <sup>2</sup>The Hamburg Centre for Ultrafast Imaging CUI, Luruper Chaussee 149, Hamburg 22761, Germany

Relative phase control with sub-cycle precision of extreme-ultraviolet (XUV) pulses from a free-electron laser has been demonstrated by

using a Michelson-type all reflective interferometric autocorrelator to trace the light-wave oscillation with a period of 129 as [1]. Novel applications using these phase controlled pulses in an electron-ion coincidence experiment will be discussed in the present contribution.

For this purpose a double-sided electron-ion coincidence spectrometer with delay-line detectors has been developed to detect electrons and ions generated in the same ionization event. The spectrometer detects ions and electrons with position-sensitivity providing angular-resolved information. The use of delay-line detectors enhances the information content of the electron spectra due to additional time-of-flight information on the ion side and thus the selection of wanted coincidence events, i.e. the selection of particularly charged ions as counterparts. First results on Xe atoms and C<sub>60</sub> molecules will be discussed.

[1] Usenko, S. et al. Attosecond interferometry with self-amplified spontaneous emission of a free electron laser. *Nat. Commun.* 8, 15626 doi: 10.1038/ncomms15626 (2017)

MO 8.4 Mon 17:15 PA 2.150

**Molecular Light-Induced Couplings Revealed by Attosecond Transient Absorption Spectroscopy** — ●LORENZ DRESCHER, GEERT REITSMA, TOBIAS WITTING, SERGUEI PATCHKOVSKII, MARC VRACKING, and JOCHEN MIKOSCH — Max-Born-Institut, Berlin, Deutschland

Attosecond transient absorption spectroscopy (ATAS) is the study of the modulation of absorption of short attosecond XUV pulses in matter by a phase-locked strong IR pulse. In recent years, ATAS has been used to study the light-induced coupling of nearby states in atoms [1] and homonuclear molecules.

Here we present results from our experimental and theoretical study of ATAS of a polyatomic molecule (CH<sub>3</sub>I) in the core-to-valence and core-to-Rydberg transition region. Core-excited states are an interesting target for transient absorption because element specific transitions give a local view into the molecular valence [2]. For ATAS they are

additionally intriguing because the short coherence time (due to fast Auger decay of the core-hole) enhances the sub-cycle dependence on the probing IR field.

Our results show the sub-cycle dependent light-induced coupling of states due to the AC Stark effect. It shows that the coupling of the core-to-Rydberg states is much stronger than the coupling of the core-to-valence states.

[1] C. Ott, et al., *Nature* 516, 374-378 (2014).

[2] L. Drescher et al., *JCP* 145, 011101 (2016).

MO 8.5 Mon 17:30 PA 2.150

**Electron spectra of a water molecule irradiated by an x-ray free-electron laser pulse** — ●JULIA M. SCHÄFER<sup>1,2</sup>, LUDGER INHESTER<sup>1,3</sup>, SANG-KIL SON<sup>1</sup>, REINHOLD F. FINK<sup>2</sup>, and ROBIN SANTRA<sup>1,3,4</sup> — <sup>1</sup>Center for Free-Electron Laser Science, DESY, Hamburg — <sup>2</sup>Institut für Physikalische und Theoretische Chemie, Universität Tübingen — <sup>3</sup>The Hamburg Center for Ultrafast Imaging, Hamburg — <sup>4</sup>Fachbereich Physik, Universität Hamburg

With the high intensity X-ray light that is generated by X-ray free-electron lasers (XFELs) molecular samples can be ionized many times. We investigate the spectrum of electrons emitted from molecules exposed to these intense X-ray pulses. Calculated photoelectron and Auger electron spectra are presented for a single water molecule that reaches through repeated ionization steps many electronic hole configurations. The rich details in the spectra depend in a non-intuitive way on X-ray pulse parameters. We discuss how the observed trends can be explained by the competition of microscopic electronic processes. A detailed comparison between spectra calculated for independent atoms and spectra calculated for molecules is made. Our results demonstrate how multiple X-ray ionization related effects like Charge-Rearrangement-Enhanced X-ray Ionization in Molecules (CREXIM) and frustrated absorption manifest themselves in the electron spectra.

## MO 9: Atomic Clusters II (joint session A/MO)

Time: Tuesday 14:00–16:00

Location: K 2.016

MO 9.1 Tue 14:00 K 2.016

**X-ray coherent diffractive imaging of quantum vortices in single helium droplets** — ●RICO MAYRO TANYAG<sup>1</sup>, CHARLES BERNANDO<sup>1</sup>, CURTIS JONES<sup>1</sup>, LUIS GOMEZ<sup>1</sup>, ANDREY VILESOV<sup>1</sup>, CAMILA BACELLAR<sup>2</sup>, JAMES CRYAN<sup>2</sup>, OLIVER GESSNER<sup>2</sup>, KEN FERGUSON<sup>3</sup>, SEBASTIAN SCHORB<sup>3</sup>, CHRISTOPH BOSTEDT<sup>3,4</sup>, DANIEL ROLLES<sup>5</sup>, and ARTEM RUDENKO<sup>5</sup> — <sup>1</sup>University of Southern California, Los Angeles, California USA — <sup>2</sup>Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California USA — <sup>3</sup>SLAC National Accelerator Laboratory, Menlo Park, California USA — <sup>4</sup>Argonne National Laboratory, Lemont, Illinois USA — <sup>5</sup>Kansas State University, Manhattan, Kansas USA

Free, single, rotating superfluid 4He nanodroplets (diameter D = 200–2000 nm, temperature T = 0.4 K) containing a number of quantum vortices have been studied via ultrafast X-ray coherent diffraction imaging using a free electron laser. The droplets were doped with Xe atoms, which collect on the vortex cores and serve as a contrast agent. In order to obtain the instantaneous positions and shapes of the vortices from the diffraction images, a phase retrieval algorithm has been developed, which utilizes the droplet boundary as a physical support. The algorithm also uses the droplet's scattering phase as an input for the iterative phase reconstruction. The obtained reconstructions reveal a plethora of transient vortex configurations within the droplet. The details of the algorithm and the possible origin of the observed vortex configuration will be discussed.

MO 9.2 Tue 14:15 K 2.016

**Imaging the equilibrium shapes of spinning superfluid quantum droplets** — ●B. LANGBEHN<sup>1</sup>, K. SANDER<sup>2</sup>, Y. OVCHARENKO<sup>1,3</sup>, C. PELTZ<sup>3</sup>, A. CLARK<sup>4</sup>, M. CORENO<sup>5</sup>, R. CUCINI<sup>5</sup>, P. FINETTI<sup>5</sup>, M. DI FRAIA<sup>5</sup>, L. GIANNESI<sup>6</sup>, C. GRAZIOLI<sup>5</sup>, D. IABLONSKYI<sup>6</sup>, A. C. LAForge<sup>7</sup>, T. NISHIYAMA<sup>8</sup>, V. OLIVER ÁLVAREZ DE LARA<sup>4</sup>, P. PISERI<sup>9</sup>, O. PLEKAN<sup>5</sup>, K. UEDA<sup>6</sup>, K. C. PRINCE<sup>5</sup>, F. STIENKEMEIER<sup>7</sup>, C. CALLEGARI<sup>5</sup>, T. FENNEL<sup>3,10</sup>, D. RUPP<sup>1,10</sup>, and T. MÖLLER<sup>1</sup> — <sup>1</sup>TU Berlin — <sup>2</sup>Univ. Rostock — <sup>3</sup>European XFEL — <sup>4</sup>EPFL, Lausanne — <sup>5</sup>Elettra-Sincrotrone Trieste — <sup>6</sup>Tohoku Univ. Sendai — <sup>7</sup>Univ. Freiburg — <sup>8</sup>Kyoto Univ. — <sup>9</sup>Univ. di Milano —

<sup>10</sup>MBI, Berlin

With the intense short-wavelength femtosecond light pulses from free-electron lasers (FELs) it is now possible to study the structure of unsupported nanoparticles, including superfluid helium nanodroplets. When produced by a free-jet expansion from the liquid phase, these droplets can gain angular momentum. As superfluid droplets cannot rotate in the classical hydrodynamic sense, quantized vortices accommodating the angular momentum are formed inside the droplets. These alter the equilibrium shapes known for normal liquid droplets. In an experiment at the FERMI FEL, we recorded wide-angle scattering images of individual helium nanodroplets. From the diffraction patterns, we reconstructed the full three-dimensional droplet shapes, enabling a comparison to a theoretical model of rotating normal liquid droplets. Surprisingly, the observed shapes of the superfluid droplets match their classical counterparts.

MO 9.3 Tue 14:30 K 2.016

**Two-color diffraction imaging of helium nanodroplets** — ●L. HECHT<sup>1</sup>, B. LANGBEHN<sup>1</sup>, Y. OVCHARENKO<sup>1,2</sup>, M. SAUPPE<sup>1</sup>, J. ZIMMERMANN<sup>1</sup>, B. KRUSE<sup>3</sup>, C. PELTZ<sup>3</sup>, K. SANDER<sup>3</sup>, A. COLOMBO<sup>4</sup>, P. PISERI<sup>4</sup>, A. D'ELIA<sup>5</sup>, M. DI FRAIA<sup>6</sup>, L. GIANNESI<sup>6</sup>, O. PLEKAN<sup>6</sup>, K. PRINCE<sup>6,7</sup>, M. ZANGRANDO<sup>6</sup>, C. CALLEGARI<sup>6</sup>, T. MÖLLER<sup>1</sup>, T. FENNEL<sup>3,8</sup>, and D. RUPP<sup>1,8</sup> — <sup>1</sup>IOAP, TU Berlin — <sup>2</sup>XFEL@DESY — <sup>3</sup>Univ. Rostock — <sup>4</sup>Univ. Milano — <sup>5</sup>Univ. Trieste — <sup>6</sup>FERMI@Elettra — <sup>7</sup>IOM, Trieste — <sup>8</sup>MBI, Berlin

Extremely intense femtosecond pulses produced by short-wavelength free-electron lasers open up the possibility to image non-depositable nanostructures like superfluid helium nanodroplets in a single shot [Gomez *et al.* *Science* **345** (2014)] and to follow the transient formation [Bostedt *et al.* *PRL* **108** (2012)] and disintegration [Gorkhovev *et al.* *Nat. Phot.* **10** (2016)] of laser-excited matter. At the FERMI facility a two-color XUV beam [Ferrari *et al.* *Nat. Comm.* **7** (2016)] can be used to perform time-resolved imaging with the goal to investigate ultrafast excitation and plasma dynamics.

Two diffraction images, each generated by one color, of the same He droplet can be separated through filter foils in front of the scattering

detector. A pulsed cryogenic cluster source produces these at a size of several hundred nanometers. A combination of around 21 and 42 eV is scanned for a resonant scattering response, as the singly ( $1s2p$ ) and doubly ( $2p3p$ ) excited states of atomic He lie close to these energies, and thereby spatially resolve the excitation profile of the nanodroplets. The experimental setup and first results will be presented.

MO 9.4 Tue 14:45 K 2.016

**Coherent diffraction images of isolated helium nanodroplets obtained with a high harmonic source** — N. MONSERUD<sup>1</sup>, B. LANGBEHN<sup>2</sup>, P. NUÑEZ VON VOIGT<sup>2</sup>, M. SAUPPE<sup>2</sup>, A. SPANIER<sup>2</sup>, J. ZIMMERMANN<sup>1,2</sup>, Y. OVCHARENKO<sup>2,3</sup>, T. MÖLLER<sup>2</sup>, F. FRASSETTO<sup>4</sup>, L. POLETTI<sup>4</sup>, A. TRABATTONI<sup>5</sup>, F. CALEGARI<sup>5,6</sup>, M. NISOLI<sup>6,7</sup>, K. SANDER<sup>8</sup>, C. PELTZ<sup>8</sup>, T. FENNEL<sup>1,8</sup>, B. SCHÜTTE<sup>1</sup>, M.J.J. VRAKING<sup>1</sup>, A. ROUZÉE<sup>1</sup>, and ●D. RUPP<sup>1,2</sup> — <sup>1</sup>Max-Born-Institut Berlin — <sup>2</sup>TU Berlin — <sup>3</sup>European XFEL — <sup>4</sup>CNR Padova — <sup>5</sup>CFEL@DESY — <sup>6</sup>CNR Milano — <sup>7</sup>Politecnico di Milano — <sup>8</sup>Universität Rostock

We recently demonstrated single-shot coherent diffractive imaging of individual gas-phase nanoparticles with a table-top light source (Nat. Comm. 8, 493 (2017)). In the present work, superfluid helium nanodroplets were irradiated by intense extreme ultraviolet (XUV) pulses from high-order harmonic generation (HHG). The single-shot XUV spectra of the multicolor pulses were measured in coincidence. From the diffraction images, a majority of spherical droplets and a small fraction of rotationally distorted prolate shapes could be identified. Further, the spherical diffraction images were analyzed via multicolor Mie fits and the refractive indices at the harmonic wavelengths were extracted. They are a sensitive measure of changes in the electronic structure and thus can serve as a handle for tracking ultrafast excitation and ionization dynamics in the droplets in time-resolved imaging approaches - ultimately with intense attosecond pulses, that are currently under development at HHG sources and free-electron lasers.

MO 9.5 Tue 15:00 K 2.016

**Machine-Learning assisted classification of diffraction images** — ●J. ZIMMERMANN<sup>1</sup>, M. SAUPPE<sup>2</sup>, B. LANGBEHN<sup>2</sup>, Y. OVCHARENKO<sup>2,4</sup>, LDM COLLABORATION<sup>3</sup>, T. FENNEL<sup>1,5</sup>, T. MÖLLER<sup>2</sup>, and D. RUPP<sup>1</sup> — <sup>1</sup>MBI Berlin — <sup>2</sup>IOAP, TU Berlin — <sup>3</sup>FERMI@Elettra — <sup>4</sup>XFEL, Hamburg — <sup>5</sup>Univ. Rostock

Short wavelength Free-Electron-Laser (FEL) enable diffractive imaging of individual nano-sized objects with a single x-ray laser shot. Due to the high repetition rates, large data sets with up to several million diffraction patterns are typically obtained in FEL particle diffraction experiments, representing a severe problem for data analysis. Assuming a dataset of  $N$  diffraction patterns with  $M \times K$  pixels, a high dimensional space ( $N \times M \times K$ ) has to be analyzed. Thus feature selection is crucial as it reduces the dimensionality. This is typically achieved via custom-made algorithms that do not generalize well, e.g. feature extraction methods applicable to spherically shaped patterns but not to arbitrary shapes. This work exploits the possibility to utilize a neural network (NN) as a feature extractor. A workflow scheme is proposed based on a Residual Convolutional NN, that drastically reduces the amount of work needed for the classification of large diffraction datasets, only a fraction of the data has to be manually classified. As a next step a generalized and fully unsupervised approach is envisioned (no manual classification needed) using an auto-encoder NN. First performance evaluations are done using data obtained from an experiment on helium nanodroplets conducted at the LDM endstation of the FERMI free-electron laser in Trieste.

MO 9.6 Tue 15:15 K 2.016

**Holography combined with iterative phase retrieval: advances in coherent diffractive imaging of single nanoparticles** — ●FELIX ZIMMERMANN<sup>1</sup>, TAIS GORKHOVER<sup>2</sup>, DANIELA RUPP<sup>1,3</sup>, THOMAS MÖLLER<sup>1</sup>, and ANATOLI ULMER<sup>1</sup> — <sup>1</sup>TU Berlin — <sup>2</sup>LCLS@SLAC — <sup>3</sup>MBI Berlin

Free-Electron-Lasers open the door to high-resolution images of non-crystallin nanoparticles such as viruses via coherent diffraction of single

X-ray pulses. The phase loss problem impedes the extraction of high resolution structural information from the recorded diffraction patterns. Two major approaches address this problem. First, one can recover the phase during post processing using iterative algorithms. Second, one can directly encode the phase into the image using reference scatterers as common in holography. The limitations and advantages of iterative and holographic methods differ significantly: iterative algorithms can reconstruct the sample from its diffraction patterns alone, but require a priori constraints and rely on human input. Usually, a number of independent reconstructions using different starting values have to be performed. The final result is based on the average of these reconstructions. In holography, a unique reconstruction without prior knowledge can be performed via simple calculations based on the Fourier transformation, but the result is degraded by the transfer function given by the reference. This talk will discuss whether a combination of both approaches might be advantageous regarding stability, computational complexity and achievable fidelity.

MO 9.7 Tue 15:30 K 2.016

**Optical focusing of isolated particles for diffractive imaging experiments** — ●SALAH AWEL<sup>1,4</sup>, DANIEL HORKE<sup>1,4</sup>, RICK KIRIAN<sup>2</sup>, XIAOYAN SUN<sup>1</sup>, ANDREI RODE<sup>3</sup>, JOCHEN KÜPPER<sup>1,4,5</sup>, and HENRY CHAPMAN<sup>1,4,5</sup> — <sup>1</sup>Center for Free-Electron Laser Science, DESY, Hamburg, Germany — <sup>2</sup>Arizona State University, Tempe, AZ, USA — <sup>3</sup>Laser Physics Centre, Australian National University, Canberra, Australia — <sup>4</sup>Center for Ultrafast Imaging, Universität Hamburg, Germany — <sup>5</sup>Department of Physics, Universität Hamburg, Germany

Single-particle imaging (SPI) is emerging as a new techniques at x-ray free-electron lasers (XFELs) that consists of directing a stream of randomly oriented bioparticles across the focus of the XFEL beam aiming to construct high-resolution 3D structure from diffraction patterns of multiple identical particles. Presently, the difficulty of efficiently delivering isolated bioparticles to the sub-micrometer x-ray focus is the limiting factor in the development of SPI. In order to mitigate this problem, we have developed a technique for guiding aerosolized nanoparticles to the x-ray focus using spatially shaped optical laser beam [1]. Our current experiments aim at transversely confining streams of aerosolized particles as they exit an aerosol injector with a counter-propagating “hollow-core” quasi-Bessel beam. Through radiation pressure and thermal (photophoretic) forces that arise from the interaction of the particle with the surrounding gas molecules, the particles confine within the low-intensity core of the laser beam [2].

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

[2] Eckerskorn et al., *Phys. Rev. Applied* **4**, 064001 (2015).

MO 9.8 Tue 15:45 K 2.016

**Signatures of Rabi cycling and excited state population dynamics in single-shot coherent diffractive imaging** — ●BJÖRN KRUSE<sup>1</sup>, CHRISTIAN PELTZ<sup>1</sup>, and THOMAS FENNEL<sup>1,2</sup> — <sup>1</sup>University of Rostock, Albert-Einstein-Straße 23, D-18059 Rostock, Germany — <sup>2</sup>Max-Born-Institute, Max-Born-Straße 2A, D-12489 Berlin, Germany

Only recently, coherent single-shot diffractive imaging (CDI) of individual free nanoparticles has been demonstrated with a laser-based source using high harmonic generation [1], promising new applications and unprecedented insights into the ultrafast dynamics induced or probed via the single-shot scattering process. So far, CDI experiments have been analyzed via an effective classical linear response description, e.g. to reconstruct the shape and orientation of nanoparticles [2]. For strong laser fields and in particular for resonant excitations, both the linear and the classical description may no longer be valid as population depletion and stimulated emission become important. To what extent such processes may influence CDI scattering images is currently largely unknown. In our theoretical analysis, we describe the quantum-mechanical few-level bound state dynamics using a density matrix formalism and incorporate this into a 3D Maxwell solver based on the finite-difference time-domain method (FDTD). We discuss how and to which extend the spatio-temporal population dynamics influences the scattering images and analyze the observed trends.

[1] D. Rupp et al., *Nat. Commun.* **8**, 493 (2017)

[2] I. Barke et al., *Nat. Commun.* **6**, 6187 (2015)

## MO 10: Strong laser fields - I (joint session A/MO)

Time: Tuesday 14:00–15:45

Location: K 2.019

**Invited Talk**

MO 10.1 Tue 14:00 K 2.019

**Multiphoton Ionization of Chiral Molecules** — ●THOMAS BAUMERT — Institut fuer Physik der Universitaet Kassel, Germany

Molecular chirality is widely recognized for its relevance to the building blocks of life and its vital role for medicine and health. Chiral recognition in the gas phase using electromagnetic radiation is an emerging research field and promising for fundamental research as well as for applications due to the non-interacting nature of molecules in the gas phase. Photoelectron angular distributions after one photon or multiphoton ionization turned out to be especially sensitive to that end and are usually measured by velocity map imaging (VMI) techniques. The corresponding circular dichroism is termed photoelectron circular dichroism (PECD). Based on electric dipole interaction, its magnitude of up to a few ten percent typically surpasses that of other chiroptical techniques and can be turned into a highly sensitive analytic tool with respect to investigation of enantiomeric excess. Resonance-enhanced multi-photon ionization (REMPI) gives access to electronic intermediates and, with the help of femtosecond laser excitation and ionization, PECD has been demonstrated on bicyclic ketones. As more angular momentum can be transferred in a multiphoton process in comparison to single photon ionization, higher order nodal structures were observed. An exploration of the nuclear and electron dynamics of the intermediate resonance may stimulate the development of laser driven purification schemes. In this talk I will present the field and our experiments. References are compiled for example in our latest publication: Kastner et al. JCP 2017, Vol. 147, 013926 (9 pp)

MO 10.2 Tue 14:30 K 2.019

**Non-linear dichroism in atomic ionization** — ●JIRI HOFBRUCKER<sup>1,2</sup>, ANDREY V. VOLOTKA<sup>1</sup>, and STEPHAN FRITZSCHE<sup>1,2</sup> — <sup>1</sup>Helmholtz Institute, Jena, Germany — <sup>2</sup>Friedrich-Schiller University Jena

Dichroic behavior is usually associated with an interaction of polarized atomic or chiral molecular target and circularly polarized light. However, in a non-linear interaction regime, elliptically polarized light ionizing symmetric target also produces a dichroic photoelectron angular distributions. The fundamental origin of this asymmetry explains why is the elliptical dichroism strictly a feature of multi-photon processes only, and why it is never observed in the single photon ionization process. Being energy and system specific, this phenomena give us an opportunity to study many-electron effects as well as fundamentals of non-linear light-matter interaction. Observation of this phenomena in two-photon ionization of an inner-shell shell electron of a rare gas atom is proposed.

MO 10.3 Tue 14:45 K 2.019

**Spin polarization and spin filtering of free electrons in bichromatic laser fields** — MATTHIAS M. DELLWEG and ●CARSTEN MÜLLER — Institut für Theoretische Physik I, Heinrich-Heine-Universität Düsseldorf

Coherent electron scattering from intense laser fields of high frequency is studied theoretically. By solving the time-dependent Dirac equation it is shown that the combination of a fundamental laser mode with a counterpropagating second harmonic may act as a spin filter for free electrons, provided the field polarizations are chosen properly [1]. Besides, a spin-polarizing interferometric electron beam splitter is presented which relies on an arrangement of three pairs of counterpropagating laser waves [2]. The proposed laser field configuration is shown to exert the same effect on free electrons as an ordinary Stern-Gerlach magnet does on atoms.

[1] M. M. Dellweg and C. Müller, Phys. Rev. A 95, 042124 (2017)

[2] M. M. Dellweg and C. Müller, Phys. Rev. Lett. 118, 070403 (2017)

MO 10.4 Tue 15:00 K 2.019

**Deterministic control with sequences of intense pulses** — ●STEFANO M. CAVALETTO, ZOLTAN HARMAN, THOMAS PFEIFER, and CHRISTOPH H. KEITEL — Max Planck Institute for Nuclear Physics, Heidelberg, Germany

Coherent-control methods and pulse-shaping technology have revolutionized our access to the quantum properties of matter. However, with widely used measurement-driven techniques, such as adaptive feedback control, the complex reaction pathways followed by an optimally controlled system often remain concealed. With intense time-dependent pulses dressing the atomic level structure, only a limited number of effective pulse-shaping strategies have been identified. Here, we put forward a deterministic scheme to fully reconstruct the action of an intense pulse on a quantum system from absorption-spectroscopy measurements, including the dependence upon possibly unknown pulse properties and atomic structures [S. M. Cavaletto *et al.*, *Phys. Rev. A* **95**, 043413 (2017)]. An optimal pulse sequence based on this extracted information can then be designed, facilitating manipulation and interpretation of the chosen control strategy. The scheme may be implemented also at x-ray energies with intense pulses from free-electron lasers, representing an effective route to x-ray quantum control.

MO 10.5 Tue 15:15 K 2.019

**Isotopic shifts measured via strong-field laser-atom interaction** — ●NICOLAS CAMUS, SOFIA BOTSIS, LUTZ FECHNER, JOSE CRESPO LÓPEZ-URRUTIA, THOMAS PFEIFER, and ROBERT MOSHAMMER — Max-Planck-Institut für Kernphysik, Saupfercheckweg 1, 69117 Heidelberg, Germany

High-precision measurements of isotopic shifts in the energy levels of atoms can provide sensitive tests of our understanding of relativistic and QED effects [1]. We present a novel spectroscopic method to measure small isotopic shifts utilizing the coherent population of different states arising from strong-field ionization. We experimentally measure the isotope shift between <sup>36</sup>Ar, <sup>38</sup>Ar and <sup>40</sup>Ar for the  $3s^2 3p^5$  ( $^2P_{3/2} \rightarrow ^2P_{1/2}$ ) transition in singly charged argon ions. We measure it by implementing a Ramsey-like scheme using two ultrashort (6 fs) laser pulses. The first laser pulse excites the system into a coherent superposition of the aforementioned states by removing an electron from the atomic p-shell of the neutral atom. This superposition leads to a spin-orbit wave packet (SOWP) oscillating with a period of  $T = 23.3$  fs that lasts for long times (tens of ns). The second delayed pulse probes, after  $\sim 170.000$  cycles, the wavepacket dynamics of the system by further ionization, allowing for a precision determination of the spin-orbit frequency at the  $\Delta E/E \sim 10^{-7}$  level. The detection of the different argon isotopes is made by a time-of-flight spectrometer. [1]. I. I. Tupitsyn *et al.*, PRA 68, 022511 (2003)

MO 10.6 Tue 15:30 K 2.019

**Two pulse characterization by interferometric imaging of self-diffraction** — ●CHRISTOPH LEITHOLD<sup>1</sup>, JAN REISLÖHNER<sup>1</sup>, HOLGER GIES<sup>2,3</sup>, and ADRIAN N. PFEIFFER<sup>1</sup> — <sup>1</sup>Institute of Optics and Quantum Electronics, Abbe Center of Photonics, Friedrich Schiller University Jena, Germany — <sup>2</sup>Theoretisch-Physikalisches Institut, Abbe Center of Photonics, Friedrich Schiller University Jena, Germany — <sup>3</sup>Helmholtz-Institut Jena, Germany

A pulse characterization scheme based on interferometric, spectrally resolved imaging of self-diffraction [1] is presented. Similar to interferometric FROG [2] and MEFISTO [3], interferograms of the nonlinear signal are recorded for different pulse delays. Due to the noncollinear nature of the setup, it can be applied to over octave spanning waveforms by separating signals on the spatial frequency axis. Additionally to the temporal waveform the method also resolves one spatial dimension and is therefore not limited by geometrical effects like beam smearing [4], known from other noncollinear schemes. In fact, both fundamental pulses can be recovered from the same measurement. The retrieval of the pulses is carried out solely in the (temporal) frequency domain and can be done analytically as well as iterative numerically which is more robust when dealing with noisy data. [1] C. Leithold, J. Reislöhner, H. Gies and A.N. Pfeiffer Opt. Lett. 42, No. 23 in press. [2] G. Stibenz and G. Steinmeyer, Opt. Express 13, 2617 (2005). [3] Amat-Roldan, I. G. Cormack, P. Loza-Alvarez, and D. Artigas, Opt. Lett. 30, 1063 (2005). [4] A. C. Tien, S. Kane, J. Squier, B. Kohler, and K. Wilson, J. Opt. Soc. Am. B 13, 1160 (1996).

## MO 11: Theoretical Approaches

Time: Tuesday 14:00–16:00

Location: PA 1.150

MO 11.1 Tue 14:00 PA 1.150

**Ab initio molecular dynamics of thiophene and its smaller oligomers: The interplay of internal conversion and intersystem crossing** — ●THOMAS SCHNAPPINGER<sup>1</sup>, PATRICK KÖLLE<sup>1</sup>, MARCO MARAZZI<sup>2</sup>, ANTONIO MONARI<sup>2</sup>, LETICIA GONZÁLEZ<sup>3</sup>, and REGINA DE VIVIE-RIEDLE<sup>1</sup> — <sup>1</sup>Department Chemie, Ludwig-Maximilians-Universität München — <sup>2</sup>TMS, SRSMC, Université de Lorraine-Nancy — <sup>3</sup>Institut für Theoretische Chemie, Universität Wien

Regarding their remarkable intrinsic properties thiophene derivatives and their oligomers are promising candidates of organic materials for technological applications for example as solar cells and light emitting diodes. A deeper understanding of the initial processes after photoexcitation and the subsequent relaxation mechanisms of oligothiophenes is an essential part to improve the performance of thiophene-based applications.

In this work we have investigated the relaxation processes after photoexcitation of thiophene, 2-2'-bithiophene and 2,2':5',2''-terthiophene. Using the SHARC ab initio surface-hopping algorithm in combination with the complete active space self-consistent field method and the time-dependent density functional theory we were able to simulate the whole relaxation including singlet and triplet states. After excitation fast ring-opening is leading the system to a degeneracy of singlet and triplet states. This situation enables fast intersystem crossing (ISC) and internal conversion (IC). The simulated relaxation pathway and the calculated time constants are in agreement with experiment.

MO 11.2 Tue 14:15 PA 1.150

**Conical Intersections and Electronic Coherence: A Novel Path to Steer Nuclear Motion** — ●CAROLINE ARNOLD<sup>1,2,3</sup>, ORIOL VENDRELL<sup>1,3,4</sup>, RALPH WELSCH<sup>1</sup>, and ROBIN SANTRA<sup>1,2,3</sup> — <sup>1</sup>Center for Free-Electron Laser Science, DESY — <sup>2</sup>Department of Physics, University of Hamburg — <sup>3</sup>The Hamburg Centre for Ultrafast Imaging — <sup>4</sup>Department of Physics and Astronomy, Aarhus University

Ultrashort pulses can be used to create coherent superpositions of electronic states in a molecule through photoexcitation. The electronic and nuclear dynamics that are triggered by the excitation are coupled in the vicinity of conical intersections (C.I.), and the Born-Oppenheimer approximation breaks down. This coupled motion provides a possibility for attochemistry, i.e., steering nuclear dynamics by controlling electronic degrees of freedom. In this work, the effect of nuclear dynamics and C.I.s on electronic coherences is investigated employing a two-state, two-mode linear vibronic coupling model. Exact quantum dynamical calculations are performed using the multi-configuration time-dependent Hartree method (MCTDH). It is found that the presence of a C.I. close to the Franck-Condon point can preserve electronic coherence to some extent. Additionally, the possibility of steering the nuclear degrees of freedom by imprinting a relative phase between the electronic states during the photoexcitation process is discussed. It is found that steering the nuclear wavepacket is possible given that a coherent electronic wavepacket embodying the phase difference passes through a C.I. A C.I. close to the Franck-Condon point is thus a necessary prerequisite for attochemistry.

MO 11.3 Tue 14:30 PA 1.150

**Non-adiabatic molecular dynamics with long-range corrected tight-binding DFT** — ●ALEXANDER HUMENIUK and ROLAND MITRIĆ — Julius-Maximilians-Universität Würzburg

The efficiency of tight-binding DFT permits non-adiabatic molecular dynamics simulation on larger systems as would be possible with full TD-DFT. However, large molecular assemblies pose new problems to DFT(B) and surface hopping, which are absent in smaller molecules: For weakly coupled chromophores, DFT with a local exchange-correlation-functional predicts unphysically low charge-transfer states. Also many degenerate electronic states appear due to excitations localized on the various identical subunits, which renders the adiabatic picture partly useless and causes numerical instabilities.

We present a software package which provides the electronic structure needed for running non-adiabatic molecular dynamics simulations at the level of charge-consistent tight-binding DFT. A long-range correction is incorporated to avoid spurious charge transfer states. Excited state energies, their analytic gradients and scalar non-adiabatic

couplings are computed using tight-binding TD-DFT. These quantities are fed into a molecular dynamics code, which integrates Newton's equations of motion for the nuclei together with the electronic Schrödinger equation. Non-adiabatic effects are included by surface hopping.

As an example, the program is applied to the optimization of excited states and non-adiabatic dynamics of polyfluorene.

MO 11.4 Tue 14:45 PA 1.150

**Improved virtual orbitals for charge transfer excitations in time dependent DFT** — ●ROLF WÜRDEMANN<sup>1</sup> and MICHAEL WALTER<sup>2,3</sup> — <sup>1</sup>FMF, Universität Freiburg, Freiburg, Germany — <sup>2</sup>FIT, Universität Freiburg, Freiburg, Germany — <sup>3</sup>IWM, Freiburg, Germany

Charge transfer excitations (CTE) are of high importance in photovoltaics, organic electronics and molecular and organic magnetism. Range separated functionals (RSF) can be used to correctly determine the energetics of CTEs within linear response time dependent density functional theory (TDDFT).

TDDFT becomes numerically very demanding on grids if hybrid or RSF are used due to the inclusion of exact exchange derived from Hartree-Fock theory.

We discuss a way to circumvent this problem by utilizing Huzinagas improved virtual orbitals (IVOs) that form an improved basis for this type of calculations. The CTE energetics may be even obtained by means of DFT ground-state calculations using IVOs.

MO 11.5 Tue 15:00 PA 1.150

**Comparison of theoretical methods for solving one-dimensional three-body problems** — ●LUCAS HAPP<sup>1</sup>, MAXIM A EFREMOV<sup>1</sup>, and WOLFGANG P SCHLEICH<sup>1,2</sup> — <sup>1</sup>Institut für Quantenphysik and Center for Integrated Quantum Science and Technology (IQ<sup>ST</sup>), Universität Ulm, D-89069 Ulm — <sup>2</sup>Hagler Institute for Advanced Study, Institute for Quantum Science and Engineering (IQSE), and Texas A&M AgriLife Research, Texas A&M University, College Station, TX 77843-4242, USA.

The well-known Born-Oppenheimer(BO) approach relies on the approximate separation of the dynamics of the light particles from that of the heavy ones which makes it suitable for systems with large mass-imbalance. On the other hand, the integral equation of Skorniakov and Ter-Martirosian (STM) provides in principle an exact description of a three-body system for any mass ratio.

In this presentation we compare both methods by solving one-dimensional three-body problems. We analyze a system of three particles with a *s*-wave resonant two-body interaction and compare the spectrum obtained via the STM method with well-known results for identical particles. In the case of a large mass-imbalance we contrast the spectrum with results of the BO approach. Finally, we extend this analysis to systems with a *p*-wave resonant two-particle interaction.

MO 11.6 Tue 15:15 PA 1.150

**Phase control of a complex Fano resonance** — ●NICOLA MAYER, MISHA IVANOV, and OLEG KORNILOV — Max Born Institut, Max-Born-Straße 2A, 12489 Berlin, Germany

A complex Fano resonance is a generic quantum mechanical system consisting of two or more autoionizing states coupled to a common continuum. This system may exhibit a counterintuitive quantum effect: an increase of the lifetime of one of these states for increasing strength of coupling to the continuum. Commonly known as interference stabilization, the effect was first proposed for laser-dressed Rydberg states [1]. In our previous work we showed that the effect takes place in the autoionization of a complex resonance in N<sub>2</sub> [2,3]. Here, we explore possibility of controlling such autoionization dynamics by changing the relative phase of two discrete states via laser-induced couplings to a third one. In particular, we show how, by inducing a phase shift of the coherent wavepacket of the two discrete states, one can control the resulting interference and selectively excite the long- or short-lived components of a complex resonance. We present theoretical calculations for transient absorption and photoelectron signals for this model system.

Reference:

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



Word Scientific, 1998. [2] M. Eckstein, N. Mayer et al., Faraday Discuss., DOI: 10.1039/C6FD00093B, 2016. [3] M. Eckstein, et al., Phys. Rev. Lett., 116, 153003, 2016.

MO 11.7 Tue 15:30 PA 1.150

**A simplified derivation of the reversal time for classical single domain ferromagnetic particles** — DECLAN BYRNE<sup>1</sup>, WILLIAM COFFEY<sup>1</sup>, YURI KALMYKOV<sup>2</sup>, and SERGEY TITOV<sup>3</sup> — <sup>1</sup>Department of Electronic and Electrical Engineering, Trinity College Dublin, Dublin 2, Ireland — <sup>2</sup>Laboratoire de Mathématiques et Physique (EA 4217), Université de Perpignan Via Domitia, F-66860, Perpignan, France — <sup>3</sup>Kotel'nikov Institute of Radio Engineering and Electronics of the Russian Academy of Sciences, Vvedenskii Square 1, Fryazino, Moscow Region 141120, Russia

It is shown, by exactly following the procedure of Kramers (H.A. Kramers, Physica 7, 284 (1940)) for escape of particles over potential barriers due to the shuttling action of the Brownian movement, how his original approach can be simply generalized to calculate the magnetization relaxation time of thermally agitated classical magnetic nanoparticles. His approach as generalized avoids the mathematical complexities associated with previous derivations. Moreover it leads to a simplified derivation of the magnetization reversal time in the

presence of spin-torque transfer.

MO 11.8 Tue 15:45 PA 1.150

**Effect of a magnetic field on molecule-solvent angular momentum transfer** — WOJCIECH RZADKOWSKI and MIKHAIL LEMESHKO — IST Austria (Institute of Science and Technology Austria), Am Campus 1, 3400 Klosterneuburg, Austria

Recently it has been shown that a molecule exchanging angular momentum with the surrounding bosonic solvent can be described in terms of the ‘angulon’ quasiparticle [1]. We now extended the angulon theory to the case of molecules possessing an additional spin-1/2 degree of freedom and studied the behavior of the system in the presence of a static magnetic field [2]. We showed that the exchange of angular momentum between the molecule and the bath can be altered by the field, even though the bath itself is not susceptible to the latter. In particular, we observed the possibility to control resonant emission of phonons with a given orbital angular momentum using a magnetic field.

[1] M. Lemeshko, Quasiparticle Approach to Molecules Interacting with Quantum Solvents, Phys. Rev. Lett. 118, 095301 (2017)

[2] W. Rzadkowski and M. Lemeshko, Effect of a magnetic field on molecule-solvent angular momentum transfer, arXiv:1711.09904

## MO 12: Cold Molecules and Reactions (joint session MO/A)

Time: Tuesday 14:00–15:45

Location: PA 2.150

### Invited Talk

MO 12.1 Tue 14:00 PA 2.150

**Towards the study of quantum-state-selected Penning reactions** — JONAS GRZESIAK, SIMON HOFSSÄSS, VIVIEN BEHRENDT, FRANK STIENKEMEIER, MARCEL MUDRICH, and KATRIN DULITZ — Institute of Physics, University of Freiburg, Hermann-Herder-Str.3, 79104 Freiburg i.Br., Germany

Our goal is to study quantum-state-controlled Penning collisions between lithium atoms and metastable helium atoms at low collision energies, e.g., to study the influence of electron-spin polarization on the reaction rate and to observe quantum resonance effects. For this, we use an experimental apparatus which consists of a discharge source for the production of metastable helium atomic beams and a magneto-optical trap (MOT) for ultracold lithium atoms. Using a novel multipulse detection scheme, we are able to mass-selectively probe the ionic reaction products at improved energy resolution. In this contribution, I will give an overview of the current state of these experiments. I will also present our progress towards achieving quantum-state selectivity of the reaction partners, which includes optical quenching of the metastable He( $2^1S_0$ ) state and magnetic-hexapole focusing of the metastable He( $2^3S_1$ ,  $M_J = 1$ ) state into the MOT target.

MO 12.2 Tue 14:30 PA 2.150

**Reactive scattering between metastable helium atoms and ultracold lithium atoms** — JONAS GRZESIAK<sup>1</sup>, VIVIEN BEHRENDT<sup>1</sup>, FRANK STIENKEMEIER<sup>1</sup>, MARCEL MUDRICH<sup>2</sup>, and KATRIN DULITZ<sup>1</sup> — <sup>1</sup>Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str.3, 79104 Freiburg i.Br. — <sup>2</sup>Department of Physics and Astronomy, Ny Munkegade 120, 8000 Aarhus C, DK

The experimental observation of quantum effects in Penning ionization reactions has recently attracted a lot of attention [1]. Our goal is to study such processes in a quantum-state-controlled manner at low collision energies, e.g., to study the influence of electron-spin polarization on the reaction rate. For this, we use an experimental setup which is composed of a magneto-optical trap for ultracold lithium atoms and a discharge source for the production of supersonic beams of metastable helium atoms. In this contribution, we will present a novel detection scheme which allows for the mass-selected detection of the ionic reaction products at improved energy resolution and we will discuss the influence of elastic collisions on the reaction rate measurements.

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

MO 12.3 Tue 14:45 PA 2.150

**Blackbody-Induced Radiative Dissociation of van der Waals Clusters at the Cryogenic Storage Ring** — FELIX NUSSLIN<sup>1</sup>, KLAUS BLAUM<sup>1</sup>, SEBASTIAN GEORGE<sup>1</sup>, JÜRGEN GÖCK<sup>1</sup>, FLORIAN GRUSSIE<sup>1</sup>, ROBERT VON HAHN<sup>1</sup>, MATTHIAS KLEIN<sup>2</sup>, THOMAS

KOLLING<sup>2</sup>, HOLGER KRECKEL<sup>1</sup>, MICHAEL LEMBACH<sup>2</sup>, CHRISTIAN MEYER<sup>1</sup>, PREETI MANJARI MISHRA<sup>1</sup>, GEREON NIEDNER-SCHATTEBURG<sup>2</sup>, VIVIANE SCHMIDT<sup>1</sup>, and ANDREAS WOLF<sup>1</sup> — <sup>1</sup>Max-Planck-Institut für Kernphysik, D-69117 Heidelberg — <sup>2</sup>Technische Universität Kaiserslautern, D-67663 Kaiserslautern

Recently, blackbody-induced dissociation of van der Waals clusters was studied for  $(SF_6)_N^-$  in a room temperature electrostatic ion beam trap [1]. However, the ground state stability of the various cluster sizes and the temperature-dependent dynamics of the infrared-active molecular clusters have not yet been investigated. For these, the Heidelberg electrostatic Cryogenic Storage Ring (CSR) provides ideal conditions. It was recently used to measure the rotational relaxation of infrared-active molecules in a  $\sim 15$  K effective radiation field [2]. Low residual gas density ( $< 140$  cm $^{-3}$ ) enables storage of fast ion beams in the CSR for times up to hours [3]. Currently, we assemble a laser vaporization source to produce  $(SF_6)_N^-$  and  $SF_6^+(SF_6)_{N-1}$  clusters. We aim at studying their heating dynamics inside the CSR at various temperatures via the two main infrared bands of  $SF_6$  at  $10.6$   $\mu m$  and  $16$   $\mu m$ .

[1] I. Rahinov et al., Eur. Phys. J. D 70 (2016) 260.

[2] C. Meyer et al., Phys. Rev. Lett. 119 (2017) 023202.

[3] R. von Hahn et al., Rev. Sci. Instrum. 87 (2016) 063115.

MO 12.4 Tue 15:00 PA 2.150

**Molecular conformer-selection by matter-wave diffraction at narrow-band optical phase gratings** — CHRISTIAN BRAND<sup>1</sup>, BENJAMIN A. STICKLER<sup>2</sup>, CHRISTIAN KNOBLOCH<sup>1</sup>, ARMIN SHAYEGHI<sup>1</sup>, KLAUS HORNBERGER<sup>2</sup>, and MARKUS ARNDT<sup>1</sup> — <sup>1</sup>Faculty of Physics, University of Vienna, Boltzmanngasse 5, A-1090 Vienna, Austria — <sup>2</sup>Faculty of Physics, University of Duisburg-Essen, Lotharstraße 1, 47048 Duisburg, Germany

Molecular conformations are of utmost importance in molecular recognition processes and recent collision studies have demonstrated the strong influence of molecular conformation on bimolecular reaction rates [1]. It is therefore of great interest to develop methods that are capable of separating single structures even from a congested conformational space. Here propose a new method that can separate conformers independently of their molecular dipole moment [2]. By diffraction the matter-wave at a near-resonant ultraviolet optical grating, individual conformers of complex molecules can be spatially isolated in a selected diffraction order. We illustrate the principle and discuss how to prepare a conformer-pure molecular beam of the neurotransmitter 2-phenylethylamine. The technique thus paves the way for structure-sensitive experiments with hydrocarbons and biomolecules, such as neurotransmitters and hormones, which evaded conformer-pure isolation so far. The applications range from environmental research, biomolecular physics to astrophysics.

[1] Chang et al., Science 342 98 (2013)



[2] C. Brand et al., ArXiv 1710.01035 (2017)

MO 12.5 Tue 15:15 PA 2.150

**Separation of water dimer** — ●HELEN BIEKER<sup>1,2</sup>, MELBY JOHNY<sup>1</sup>, THOMAS KIERSPEL<sup>1</sup>, BORIS SARTAKOV<sup>3</sup>, ANDREY YACHEMENEV<sup>1</sup>, SEBASTIAN TRIPPEL<sup>1,3</sup>, DANIEL A. HORKE<sup>1,2</sup>, and JOCHEN KÜPPER<sup>1,2,4</sup> — <sup>1</sup>Center for Free-Electron Laser Science, DESY — <sup>2</sup>The Hamburg Center for Ultrafast Imaging, University Hamburg — <sup>3</sup>General Physics Institute, Russian Academy of Sciences — <sup>4</sup>Department 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 separation of water dimer in strong electric fields, extending previous studies [2].

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 12.6 Tue 15:30 PA 2.150

**A Molecular Zeeman slowing scheme** — ●MAURICE PETZOLD, PAUL KAEBERT, PHILIPP GERSEMA, MIRCO SIERCKE, and SILKE OSPELKAUS — Institut für Quantenoptik, Leibniz Universität Hannover

We present our results on implementing a novel technique for slowing molecules to velocities trappable by magneto-optical traps. The scheme relies on the decoupling of angular momenta at high magnetic fields and is capable of continuously slowing and compressing the 1D velocity distribution. Detailed Monte-Carlo simulations show a significant increase in flux of slow molecules compared to current slowing techniques. To underline our theoretical efforts, we perform an experiment on an atomic test bed with similar level structure, showing good agreement between experimental and theoretical results. The advantages and implementation of our scheme closely resemble those of atomic Zeeman slowing, and implementation of our idea in a molecular system could be the missing link for realizing a large, ultra-cold ensemble of directly cooled molecules.

## MO 13: Posters 1: Ultrafast Spectroscopy

Time: Tuesday 16:15–18:15

Location: Orangerie

MO 13.1 Tue 16:15 Orangerie

**Multidimensional electronic spectroscopy with mass-resolved ion detection** — ●HANS-PETER SOLOWAN, TRISTAN FORD, SEBASTIAN ROEDING, and TOBIAS BRIXNER — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

We report a new technique, molecular-beam coherent two-dimensional (2D) electronic spectroscopy, enabling multidimensional electronic spectroscopy of gas-phase samples with mass-resolved ion detection. Using time-of-flight mass spectrometry, we have introduced cations as a new observable in coherent 2D spectroscopy.

Using a pulse shaper based on an acousto-optic programmable dispersive filter and rapid scanning [1] we focus a train of four collinear pulses in the visible regime into an interaction region with a molecular beam. Via phase cycling [2] the signals of the time-of-flight mass spectrometer can be disentangled to extract the different contributions, like the photon-echo response. With this new experimental method, the ionization pathway of nitrogen dioxide is investigated and the first ion-selective 2D spectrum of a molecular-beam sample is acquired. By implementation of a supersonic molecular beam with argon as a seed gas, the range of potential samples will be extended.

[1] S. Draeger, S. Roeding, and T. Brixner, *Opt. Express* **25**, 3259 (2017)

[2] H.-S. Tan, *J. Chem. Phys.* **129**, 124501 (2008).

MO 13.2 Tue 16:15 Orangerie

**Setup of a transportable monolithic platform for phase-modulated UV wave-packet interferometry** — ●LARS-STEPHAN KLEIN, ANDREAS WITUSCHEK, LUKAS BRUDER, and FRANK STIENKEMEIER — Universität Freiburg, Physikalisches Institut, Hermann-Herder-Str. 3, 79104 Freiburg, Germany

Coherent time-resolved spectroscopy allows the precise analysis of ultrafast dynamics in complex systems. Using short UV wavelengths would provide new opportunities for studying electronic excitations in molecular systems. However, the practical realization poses high demands on interferometric stability. In our approach, we use acousto-optical (AO) phase-modulation to ease demands on stability and to isolate weak nonlinear signals from huge backgrounds. We present a transportable monolithic platform for the interferometer including high-efficiency AO modulators with large apertures due to high pulse powers. A cw-laser is used as reference tracer which is needed at low repetition rates, as well as transversally driven fused-silica wedges as a delay unit. This makes the setup suitable for seed laser beamlines of free electron lasers where long beam paths to the undulator cannot be avoided.

MO 13.3 Tue 16:15 Orangerie

**Broadband rapid-scan coherent 2D fluorescence spectroscopy** — STEFAN MÜLLER, ●SIMON DRAEGER, XIAONAN MA, MATTHIAS HENSEN, and TOBIAS BRIXNER — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

We developed an all-collinear setup for 2D electronic spectroscopy using fluorescence as an observable. The supercontinuum output of an argon-filled hollow-core fiber is used for broadband excitation in the visible spectral range. The pulse trains are generated and varied by an acousto-optic dispersive filter on a 1 kHz shot-to-shot basis, thus enabling rapid data acquisition. We show that it is possible to obtain 2D spectra within a few seconds, containing various nonlinear contributions such as photon echo and two-quantum coherences. Furthermore, we provide a detailed description of the underlying Liouville pathways that give rise to those nonlinear contributions, and show how to extract them experimentally with three- and four-pulse sequences via phase cycling.

MO 13.4 Tue 16:15 Orangerie

**Photophysics of molecular systems studied by THz emission spectroscopy** — ●PHILIPP KRAUSPE and NATALIE BANERJI — University of Bern Department of Chemistry and Biochemistry, Freiestrasse 3, 3012 Bern

Terahertz Emission Spectroscopy (TES) is a versatile technique to monitor ultrafast processes in material systems such as Dichalcogenides, Perovskites, Semiconductors or organic semiconductors which are the focus of this work. With TES we can monitor ultrafast electronic processes through the emission of photons in the THz frequency range. Therefore we subject the material system to an external bias field and excite it with an ultrashort light pulse (35 fs).

Electric field sensitive species within the material are accelerated by the bias field and thus create the THz waveform which is subsequently probed with electro-optic sampling (EOS).

In contrast to optical pump THz probe spectroscopy the time resolution in TES is not limited by the duration of the THz probe pulse but by the gating pulse in the EOS. We use this advantage to resolve the charge generation mechanisms on a sub picosecond timescale.

MO 13.5 Tue 16:15 Orangerie

**Transient Absorption Spectroscopy of a Photochromic Coordination Cage** — ●KEVIN ARTMANN<sup>1</sup>, RUJIN LI<sup>2</sup>, SIMON SCHULKE<sup>1</sup>, GUIDO H. CLEVER<sup>2</sup>, and PATRICK NUERNBERGER<sup>1</sup> — <sup>1</sup>Physikalische Chemie II, Ruhr-Universität Bochum, 44780 Bochum — <sup>2</sup>Anorganische Chemie, Technische Universität Dortmund, 44227 Dortmund

Coordination cages have auspicious applications due to their ability to encapsulate guest compounds selectively. Recently, Han *et al.* established a photochromic coordination cage for which uptake and release of the guest molecule can be triggered by light [1]. The cage is composed of two square-planar-coordinated Pd<sup>2+</sup> ions and four bis-monodentate pyridyl ligands based on a dithienylethene (DTE) photoswitch. UV excitation may initiate a ring-closure of the DTE ligand and traps the guest inside the cage. In this study, we demonstrate that the ultrafast photodynamics of the single ligand in solution are similar to those of a closely related DTE derivative examined by Ern *et al.* [2]. However, the metal-organic coordination cage shows significant differences in its photodynamics compared to the ligand building blocks. Whereas the ground-state bleach almost completely recovers within a few ps after excitation of the closed DTE ligand, it persists for the accessible time range of several ns in the case of the closed coordination cage.

\*[1] Han *et al.*, *Angew. Chem. Int. Ed.* 2013, 52, 1319-1323.

\*[2] Ern *et al.*, *J. Phys. Chem. A* 2001, 105, 1741-1749.

MO 13.6 Tue 16:15 Orangerie

**Quantum Chemical Study of a Super-Photoacid** — ●NIKLAS SUELZNER and CHRISTOF HÄTTIG — Arbeitsgruppe Quantenchemie, Ruhr-Universität Bochum, 44780 Bochum

Photoacidity, i.e. the increase of acidity upon photo-excitation, is a common feature of aromatic alcohols. Depending on the ring's substituents, the strength of a photoacid may vary significantly which, in turn, initiated the discussion of different mechanism for excited-state proton transfer (ESPT). Frequently mentioned molecular origins of photoacidity include intramolecular charge redistribution (charge transfer), hydrogen bonding and solvent interactions.

Accompanying the experimental work on hydroxypyrene-tris(hexafluoropropylsulfonate), we performed a detailed quantum chemical study on this super-photoacid using the wavefunction-based methods ADC(2) and CC2 together with the solvation model COSMO for the treatment of bulk solvation effects. We aimed at gaining insights into the electronic structure and the structural changes occurring upon electronic excitation. The protonated and deprotonated forms were treated separately and in addition, a water complex was investigated. Our results clearly indicate a contribution of charge redistribution in the first excited-state as well as hydrogen bonding to solvent molecules, in accordance with the experimental electronic spectra.

MO 13.7 Tue 16:15 Orangerie

**The Effect of Water on the Dynamics of a Superphotoacid in Acetone–Water Mixtures** — ●NIKLAS SUELZNER<sup>1</sup>, BASTIAN GEISSLER<sup>1</sup>, JOHANNES KNORR<sup>1</sup>, CHRISTIAN SPIES<sup>1</sup>, BJÖRN FINKLER<sup>2</sup>, GREGOR JUNG<sup>2</sup>, and PATRICK NUERNBERGER<sup>1</sup> — <sup>1</sup>Physikalische Chemie II, Ruhr-Universität Bochum, 44780 Bochum — <sup>2</sup>Biophysikalische Chemie, Universität des Saarlandes, 66123 Saarbrücken

Photoacids exhibit a higher tendency to transfer an acidic proton in their electronically excited state compared to the ground state, which can trigger an excited-state proton transfer (ESPT). Using time-resolved spectroscopy, the ESPT process can be investigated on its actual timescale. Previous studies disclosed that the particularly strong photoacid hydroxypyrene-tris(hexafluoropropylsulfonate) is capable of performing an ESPT even in the weakly basic solvent acetone. The role of water acting as an impurity in such aprotic, polar solvents remained unsettled though and might have a severe effect.

In this study, the influence of water on the ESPT of this photoacid in acetone–water mixtures was scrutinized by use of time-resolved streak camera fluorescence spectroscopy. Acetoneous samples with linearly increasing amounts of water (0 – 5 %) revealed a significant enhancement of the ESPT rate by nearly one order of magnitude. A further study on the alternating effect of adding water and acidifying the solution demonstrated that the observed ESPT acceleration was partially reversible. We infer that the water molecules act as acceptors facilitating the proton transfer but can be passivated by acidification.

MO 13.8 Tue 16:15 Orangerie

**Ultrafast relaxation dynamics of [Fe(CN)<sub>6</sub>]-3 studied by means of transient absorption and XUV photoemission spectroscopy** — ●AZHR ABDULZAHRAA RAHEEM<sup>1,2</sup>, NATALIA KUZKOVA<sup>1,2</sup>, CHRISTOPH MERSCHJANN<sup>1,2</sup>, and IGOR KIYAN<sup>1,2</sup> — <sup>1</sup>Institute of Methods for Material Development, Helmholtz-zentrum Berlin, Albert-Einstein-Str. 15 12489 Berlin Germany — <sup>2</sup>Department

of Physics, Freie Universität Berlin, Arnimallee 14, 14195, Berlin, Germany

We investigate light-induced structural changes and relaxation dynamics of ferricyanide, [Fe(CN)<sub>6</sub>]-3, in aqueous solution using ultrafast transient photoelectron and absorption spectroscopy. The relaxation mechanism of [Fe(CN)<sub>6</sub>]-3 has recently received contradictory interpretations. With the use of transient XUV photoemission spectroscopy [1], a two-step ultrafast relaxation following the initial optical ligand-to-metal charge-transfer was revealed. Another study reported on monoexponential ultrafast decay followed by an additional long-lived signal [2]. We performed experiments with two configurations, where we applied perpendicular and magic-angle polarization orientations. Our results confirm the ultrafast double-exponential decay of the excited electron population, as well as the presence of a long-lived state. [1] N. Engel, S. I. Bokarev, A. Moguilevski, A. A. Raheem, R. Al-Obaidi, T. Möhle, G. Grell, K. R. Siefertmann, B. Abel, S. G. Aziz, O. Kühn, M. Borgwardt, I. Yu. Kiyann and E. F. Aziz, *Phys.Chem.Chem.Phys.*, 2017, 19, 14248. [2] J. Ojeda, C. A. Arrell, L. Longetti, M. Chergui and J. Helbing, *Phys.Chem.Chem.Phys.*, 2017, 19, 17052.

MO 13.9 Tue 16:15 Orangerie

**Disentangling the different time scales in the photodynamics of the molecular rotor molecule Thioflavin T** — ●BASTIAN GEISSLER, KEVIN ARTMANN, and PATRICK NUERNBERGER — Physikalische Chemie II, Ruhr-Universität Bochum, 44780 Bochum

In the dye Thioflavin T (ThT), a benzothiazole (BTA) cation is linked to N,N-dimethylaniline (DMA) via a freely rotatable bond. When excited, this rotation can lead to ultrafast deactivation, while the fluorescence yield strongly increases if this rotation is hindered, which is why ThT is a popular marker for protein aggregation and amyloid fibril formation. Moreover, the fluorescence lifetime of ThT can also vary from ps up to ns depending on the excitation wavelength, as a consequence of the pre-rotation angle between the BTA and DMA moieties in the ground state. An initially planar ThT molecule deactivates within ps because of excited-state twisting, whereas an initially pre-twisted ThT molecule shows no excited-state rotational motion and is thus long-lived. Previous work disclosed that the long-lived fluorescence originates from the BTA moiety of the dye. In this study, we performed ultrafast spectroscopy via fluorescence streaking and transient absorption in the UV spectral range for ThT and its building blocks DMA and BTA in various solvents and with different pH values. While the pre-twisted and planar ThT configurations can be selectively excited below and above 400 nm, respectively, leading to pronounced differences in the photodynamics, deep-UV excitation below 300 nm leads to no selectivity. The long-lived emission of ThT can be associated with the ns lifetime observed for BTA.

MO 13.10 Tue 16:15 Orangerie

**Towards understanding the mechanism of water splitting on TiO<sub>2</sub>** — SAMAN HOSSEINPOUR, SIMON J. SCHLEGEL, MISCHA BONN, and ●ELLEN H.G. BACKUS — Max Planck Institute for Polymer Research, Mainz, Germany

Finding a clean and renewable energy source to replace fossil fuels has attracted much attention, the past few decades, as a requirement for the sustainable development of societies. Direct hydrogen generation on TiO<sub>2</sub> by photocatalytic dissociation of water using sunlight was first proposed over 40 years ago. However, despite extensive work in this area, the fundamentals of the process remain ill-understood, mainly due to the lack of a proper tool to specifically explore the interface between water and TiO<sub>2</sub>. Sum frequency generation spectroscopy (SFG), is an inherently surface sensitive tool, allowing the study of the water-TiO<sub>2</sub> interface. We show time-resolved SFG data after excitation of TiO<sub>2</sub> with a femtosecond UV pump pulse, which mimics the sunlight. Preliminary data show that both the surface and the interfacial water molecules undergo changes on ultrafast timescales upon excitation. These UV-pump SFG-probe data illustrate the first steps towards following the photo-induced dissociation of water at the TiO<sub>2</sub> interface in real-time.

MO 13.11 Tue 16:15 Orangerie

**Ultrafast processes in luminescent mono- and dinuclear copper(I)-complexes** — ●MERTEN GRUPE<sup>1</sup>, FLORIAN BÄPPLER<sup>1</sup>, MANUEL ZIMMER<sup>2</sup>, STEFAN BRÄSE<sup>3</sup>, MARKUS GERHARDS<sup>2</sup>, and ROLF DILLER<sup>1</sup> — <sup>1</sup>Dept. of Physics, TU Kaiserslautern, 67663 Kaiserslautern — <sup>2</sup>Dept. of Chem., TU Kaiserslautern, 67663 Kaiserslautern — <sup>3</sup>Dept. of Org. Chem., KIT, 76131 Karlsruhe

Copper(I)-complexes play a crucial role for the design of efficient and sustainable light emitters. To get a profound understanding of luminescence, controlled by photoinduced intra- and intermolecular processes, such as molecular flattening, intersystem crossing, solvation etc. we employed femtosecond UV/Vis transient absorption (TA) on mono<sup>[1]</sup>- and dinuclear<sup>[2][3][4]</sup> copper(I)-complexes. The results allow a rigorous comparison of the respective ultrafast dynamics in solution and solid phase, possibly controlled by metal-metal cooperativity. For the elucidation of molecular flattening we employed femtosecond mid-IR TA on a heteroleptic mononuclear copper(I)-complex.

- [1] L. Bergmann et al. Chem. Commun., 2013, 49 6501
- [2] F. Böppler et al. PCCP, 2017
- [3] D. Volz et al. Chem. Mater., 2013
- [4] Wallesch et al. Chem. Eur. J., 2016

MO 13.12 Tue 16:15 Orangerie

**Excitonic Coupling and Energy Transfer in the LH2 Complex of Allochromatium Vinosum** — ●MARCO SCHRÖTER<sup>1</sup>, MARCELO ALCOCCER<sup>2</sup>, OLIVER KÜHN<sup>1</sup>, and DONATAS ZIGMANTAS<sup>2</sup> — <sup>1</sup>Institut für Physik, Universität Rostock, Albert-Einstein-Str. 23-24, 18059 Rostock, Germany — <sup>2</sup>Chemical Physics, Lund University, Box 124, 22100 Lund, Sweden

Bacterial photosynthesis is one of the most adaptable and robust energy harvesting processes in nature, with light-harvesting complexes playing a crucial role. The peripheral light-harvesting complex (LH2) of the purple bacterium *Allochromatium vinosum* is particularly distinct as it shows a double peak structure in the B800 absorption band. Two hypotheses concerning the origin of this splitting have been proposed; either two distinct B800 bacteriochlorophyll site energies [1], or an excitonic dimerization of bacteriochlorophylls within the B800 ring [2]. Through the use of two-dimensional electronic spectroscopy, we present unambiguous evidence that the peak splitting is due to the latter. Furthermore, we identify and characterize all energy transfer pathways within this complex by using a refined global fitting procedure [3]. Our approach demonstrates how the combination of two-dimensional spectral resolution and self-consistent fitting allows for the extraction of information on light-harvesting processes, which would otherwise be inaccessible due to signal congestion.

[1] D. M. Niedzwiedzki et al., Biochim. Biophys. Acta 1817, 1576 (2012) [2] A. Löhrner et al., Photosynth. Res. 123, 23 (2015) [3] J. Dostal et al., J. Chem. Phys. 145, 124312 (2016)

MO 13.13 Tue 16:15 Orangerie

**Ultrafast Transient Reflectivity on Metal Complexes** — ●FLORIAN BÄPPLER<sup>1</sup>, MERTEN GRUPE<sup>1</sup>, LARS SCHÜSSLER<sup>1</sup>, CHRISTOPH RIEHN<sup>1,2</sup>, and ROLF DILLER<sup>1</sup> — <sup>1</sup>TU Kaiserslautern, 67663 Kaiserslautern, Germany — <sup>2</sup>Forschungszentrum OPTIMAS, 67663 Kaiserslautern, Germany

Photophysical properties can be drastically altered by the sample parameters, e.g. packing density, solid state, gas phase, solvent and temperature. Therefore, in order to optimize device efficiency and functionality, it is critical to investigate the sample in the same environment as in the application. Femtosecond transient absorption (fs-TA) in transmission is a well established method to study ultrafast photophysical processes in molecules. This method is limited to transparent samples.

However, for non-transparent samples such as crystals and pressed pellets, femtosecond transient reflectivity (fs-TR) can give unique insights into the ultrafast dynamics upon photoexcitation. Here, we present a recent study comparing photophysical dynamics of the binuclear OLED-emitter Cu<sub>2</sub>I<sub>2</sub>MePyrPHOS<sup>[1]</sup> in solution, film and as pressed neat pellet, using both fs-TA alongside with fs-TR. A perspective on how fs-TR as a tool to investigate metal complexes can be applied and improved is given.

- [1] F. Böppler et al. PCCP, 2017

MO 13.14 Tue 16:15 Orangerie

**Multi-state Photoelectron Circular Dichroism in Femtosecond Multiphoton Ionization** — ALEXANDER KASTNER<sup>1</sup>, TOM RING<sup>1</sup>, ●ROXANA SAVULEA<sup>1</sup>, BASTIAN C. KRÜGER<sup>2</sup>, G. BARRATT PARK<sup>2</sup>, TIM SCHÄFER<sup>2</sup>, ARNE SENFTLEBEN<sup>1</sup>, and THOMAS BAUMERT<sup>1</sup> — <sup>1</sup>Universität Kassel, Institut für Physik und CINSaT, D-34132 Kassel, Germany — <sup>2</sup>Institut für Physikalische Chemie, Georg-August-Universität Göttingen, D-37077 Göttingen, 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]. Due to the multi-photon ionization, we observed highly structured asymmetries with a magnitude in the range of  $\pm 10\%$  on bicyclic Ketones [3, 4]. By scanning the laser excitation wavelength, up to three electronically distinct resonances can be simultaneously populated. The intermediate state and the excitation wavelength define the photoelectron energy. We report on the dependence of magnitude and sign of PECD on photoelectron energy [5].

- [1] I. Powis, 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)
- [5] A. Kastner et al., J. Chem. Phys. 147, 013926, (2017)

MO 13.15 Tue 16:15 Orangerie

**Time-resolved photoelectron circular dichroism in solution** — ●JANINA LEBENDIG-KUHLE, HANS-HERMANN RITZE, and ANDREA LÜBCKE — Max-Born-Institut für Nichtlineare Optik und Kurzzeit-spektroskopie, Berlin

The phenomenon of chirality is a widely spread characteristic of molecules, especially in biological systems. This property is accompanied by circular dichroism, the effect of a chiral molecule interacting differently with circularly polarized light of different handedness. We combine time-resolved photoelectron circular dichroism (TR-PECD) measurements with the liquid jet technique to investigate the excited state dynamics of chiral molecules in solution. This method implies the generation of ultrashort circularly polarized UV-pulses as well as a detection scheme compatible with the liquid jet environment. We will present our experimental approach and show first results.

MO 13.16 Tue 16:15 Orangerie

**Generating laser-pulse enantiomers** — ANDREAS STEINBACHER<sup>1,2</sup>, ●HEIKO HILDENBRAND<sup>1</sup>, SEBASTIAN SCHOTT<sup>1</sup>, JOHANNES BUBACK<sup>1</sup>, MARCO SCHMID<sup>1</sup>, PATRICK NUERNBERGER<sup>3</sup>, and TOBIAS BRIXNER<sup>1</sup> — <sup>1</sup>Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg — <sup>2</sup>Department of Chemistry, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139, USA — <sup>3</sup>Physikalische Chemie II, Ruhr-Universität Bochum, 44780 Bochum

We developed an optical setup capable of mirroring an arbitrary, potentially time-varying, polarization state of an ultrashort broadband laser pulse [1]. This is achieved by splitting up the incident beam in two separate beams of which one is mirrored by reflection off a mirror in normal incidence. Afterwards, both beams are recombined in time and space such that two collinearly propagating ultrashort laser pulses with mutually mirrored polarization, i.e., laser-pulse enantiomers, leave the setup. Via this approach, wave plates are not needed and broadband pulses in a large wavelength range can be processed.

Since the two beams travel separately through the optical system, shot-to-shot chopping and detection schemes can be applied. These capabilities are desired, e.g., for circular dichroism, ellipsometry, anisotropy or chiral quantum control experiments. As an application example, the latest progress on time-resolved circular dichroism and transient absorption spectroscopy on the early photochemistry of oxygenated myoglobin is presented.

- [1] Steinbacher et al., Opt. Express 25, 21736 (2017)

MO 13.17 Tue 16:15 Orangerie

**First results of XUV transient absorption spectroscopy in the ionization continuum of molecular hydrogen** — ●GERGANA D. BORISOVA, PAUL BIRK, VEIT STOOSS, MAXIMILIAN HARTMANN, ALEXANDER BLÄTTERMANN, NIKOLA MOLLOV, ROBERT MOSHAMMER, CHRISTIAN OTT, and THOMAS PFEIFER — Max-Planck-Institut für Kernphysik, Heidelberg

In studies of the ionization dynamics in atoms and molecules after light-matter interaction, usually electrons and/or ions are detected, as they are the natural products of the ionization process. Investigating ionization dynamics in molecular hydrogen is therefore predominantly done by measuring charged particles [1]. Here, we experimentally consider the complementary approach of attosecond transient-absorption spectroscopy (ATAS) and aim at the energy region around the Qn doubly excited resonances. First results of this technically challenging experiment will be presented, with emphasis on a systematic study of various obstacles that arise when searching for weak and broadband spectral signatures in an ATAS experiment.

- [1] Palacios et al., J. Phys. B: At. Mol. Opt. Phys. 48, (2015)

242001

MO 13.18 Tue 16:15 Orangerie

**pump-probe experiments with molecules at FLASH** — ●YIFAN LIU<sup>1</sup>, KIRSTEN SCHNORR<sup>1</sup>, GEORG SCHMID<sup>1</sup>, SVEN AUGUSTIN<sup>1</sup>, SEVERIN MEISTER<sup>1</sup>, HANNES LINDENBLATT<sup>1</sup>, THOMAS DING<sup>1</sup>, YUHAI JIANG<sup>2</sup>, ROLF TREUSCH<sup>3</sup>, STEFAN DÜSTERER<sup>3</sup>, MATHIEU GISELBRUCH<sup>4</sup>, CHRISTIAN BURGER<sup>5</sup>, MATTHIAS KUEBEL<sup>5</sup>, MATTHIAS KLING<sup>5</sup>, ARTEM RUDENKO<sup>6</sup>, CLAUS DIETER SCHROETER<sup>1</sup>, THOMAS PFEIFER<sup>1</sup>, and ROBERT MOSHAMMER<sup>1</sup> — <sup>1</sup>Max-Planck-Institut für Kernphysik, Saupfercheckweg 1, Heidelberg, 69117, Germany — <sup>2</sup>Shanghai Advanced Research Institute, Zhangjiang, Shanghai, 201210, China — <sup>3</sup>Deutsches Elektronen-Synchrotron, Notkestrasse 85, 22607, Hamburg, Germany — <sup>4</sup>Lund University, Lund, Post Box 118, 22100, Sweden — <sup>5</sup>Max Planck Institute of Quantum Optics, Hans-Kopfermann-Straße 1, D-85748 Garching, Germany — <sup>6</sup>J. R. Macdonald Laboratory, Department of Physics, Kansas State University, Manhattan, Kansas, 66506, USA

With a pump-probe experimental scheme, the ultrafast temporal resolution molecular dynamics of N<sub>2</sub> and O<sub>2</sub> were investigated at the Free-Electron-LASer in Hamburg (FLASH). Firstly, IR-assisted XUV multiphoton experiment of N<sub>2</sub> was performed at FLASH in combination with a synchronized femtosecond optical laser. The fragmentation and multiple ionization dynamics of N<sub>2</sub> have been investigated using a Reaction-Microscope (ReMi). We find the sequential ionization is to be the dominant and efficient process for molecules in X-ray regime. The second experiment is that we use the THz electric field to trace the autoionization process happening in molecular oxygen.

MO 13.19 Tue 16:15 Orangerie

**Studies of atomic and molecular dynamics with few-femtosecond XUV and IR fields** — LORENZ DRESCHER, GEERT REITSMA, TOBIAS WITTING, MARC VRAKING, and ●JOCHEN MIKOSCH — Max-Born-Institute, Max-Born-Strasse 2A, 12489 Berlin

Atomic and molecular dynamics on attosecond and few-femtosecond timescales can be studied using a number of different protocols involving few-cycle infrared (IR) pulses and extreme ultraviolet (XUV) pulses from High Harmonic Generation.

Here we showcase the results from three different experiments performed with the same versatile experimental apparatus:

(1) The few-femtosecond passage of conical intersections in benzene was studied with time-resolved photofragment spectroscopy. The dynamics represent one of the fastest internal conversion processes in a molecule studied to date and allow for a detailed comparison with multi-configurational time-dependent Hartree calculations [1].

(2) We analyze the XUV-IR induced excitation of neutral states in helium by UV photoelectron spectroscopy. The observed oscillation of the 1s<sub>3p</sub> population with the XUV-IR phase is assigned to the superposition of two independent two-color two-pathway interferences, which are out-of-phase.

(3) Finally, we present results from attosecond transient absorption spectroscopy of CH<sub>3</sub>I molecules in the core-to-valence and core-to-Rydberg transition region. Our results show the sub-cycle dependent

light-induced coupling of these states due to the AC Stark effect.

[1] Galbraith et al., Nature Comm. **8**, 1018 (2017)

MO 13.20 Tue 16:15 Orangerie

**All-XUV transient-absorption spectroscopy on the ultrafast dissociation of small molecules** — ●MARC REBHOLZ<sup>1</sup>, THOMAS DING<sup>1</sup>, LENNART AUFLEGER<sup>1</sup>, MAXIMILIAN HARTMANN<sup>1</sup>, ALEXANDER MAGUNIA<sup>1</sup>, DAVID WACHS<sup>1</sup>, KRISTINA MEYER<sup>1</sup>, VEIT STOOSS<sup>1</sup>, PAUL BIRK<sup>1</sup>, GERGANA BORISOVA<sup>1</sup>, CARINA DA COSTA CASTANHEIRA<sup>1</sup>, PATRICK RUPPRECHT<sup>1</sup>, ANDREW ATTAR<sup>2</sup>, ZHI HENG LOH<sup>3</sup>, THOMAS GAUMNITZ<sup>4</sup>, SEBASTIAN ROLING<sup>5</sup>, MARCO BUTZ<sup>5</sup>, HELMUT ZACHARIAS<sup>5</sup>, STEFAN DÜSTERER<sup>6</sup>, ROLF TREUSCH<sup>6</sup>, VICTOR DESPRÉ<sup>7</sup>, ALEXANDER KULEFF<sup>7</sup>, CHRISTIAN OTT<sup>1</sup>, and THOMAS PFEIFER<sup>1</sup> — <sup>1</sup>Max-Planck Institut für Kernphysik, Heidelberg, Germany — <sup>2</sup>University of California Berkeley, Berkeley, USA — <sup>3</sup>Nanyang Technological University Singapore, Singapore — <sup>4</sup>Eidgenössische Technische Hochschule Zürich, Zürich, Switzerland — <sup>5</sup>Westfälische Wilhelms-Universität Münster, Münster, Germany — <sup>6</sup>Deutsches Elektronen-Synchrotron (DESY), Hamburg, Germany — <sup>7</sup>Universität Heidelberg, Heidelberg, Germany

We present first results of a transient-absorption experiment using only extreme ultraviolet (XUV) light. The XUV laser pulses with photon energies near 50 eV and pulse durations of ~ 50 fs are provided by the free-electron laser FLASH. This allows us to pump a core-electron transition (4d → σ\*) in the target molecules methyl iodide (MEI) and diiodomethane (DIM) with high-intensity (estimated 10<sup>14</sup> W/cm<sup>2</sup>) XUV light. We investigate the subsequent ultrafast dissociation by tracing changes in the absorption spectrum of an identical XUV probe pulse.

MO 13.21 Tue 16:15 Orangerie

**Ultrafast electronic delay of core excited HCl molecules measured with THz streaking** — ●KATHARINA WENIG<sup>1</sup>, MAREK WIELAND<sup>1</sup>, SOPHIE WALTHER<sup>1</sup>, ARNE BAUMANN<sup>1</sup>, ANATASIOS DIMITRIOU<sup>1</sup>, MARK PRANDOLINI<sup>1</sup>, OLIVER SCHEPP<sup>1</sup>, IVETTE BERMÚDEZ MACHIAS<sup>2</sup>, MALTE SUMFLETH<sup>1</sup>, NIKOLA STOJANOVIC<sup>2</sup>, STEFAN DÜSTERER<sup>2</sup>, JULIANE RÖNTSCH-SCHULENBURG<sup>2</sup>, MARKUS DRESCHER<sup>1</sup>, and ULRIKE FRÜHLING<sup>1</sup> — <sup>1</sup>Institut für Experimentalphysik, Universität Hamburg, Deutschland — <sup>2</sup>Deutsches Elektronen-Synchrotron DESY, Hamburg, Deutschland

We have resonantly excited 2p<sub>3/2</sub> core electrons from HCl molecules to the antibonding σ\* orbital using femtosecond soft-x-ray pulses from the free-electron laser in Hamburg (FLASH). After the excitation the molecules dissociate and the electronic excitation relaxes via the emission of an Auger-electron. Both processes compete on similar ultrashort femtosecond time scales. In order to follow the evolution of this coupled electronic and nuclear dynamics, we equipped x-ray electron spectroscopy with time resolution.

In our experiment the exciting soft-x-ray pulses were collinearly superimposed with intense THz pulses from the FLASH THz undulator. Electrons emitted from the molecules are accelerated (streaked) by the THz electric field whereby the resulting momentum change depends on the THz phase at the instant of ionization. The experimental setup and first experimental results will be presented.

## MO 14: Atomic Clusters III (joint session A/MO)

Time: Wednesday 14:00–15:30

Location: K 2.016

MO 14.1 Wed 14:00 K 2.016

**Single-shot electron imaging of helium nanoplasmas** — ●DOMINIK SCHOMAS<sup>1</sup>, NICOLAS RENDLER<sup>1</sup>, ANDREAS HEIDENREICH<sup>2,3</sup>, THOMAS PFEIFER<sup>4</sup>, ROBERT MOSHAMMER<sup>4</sup>, and MARCEL MUDRICH<sup>5</sup> — <sup>1</sup>Physikalisches Institut, Albert-Ludwigs-Universität, Freiburg — <sup>2</sup>Kimika Fakultatea, Euskal Herriko Unibertsitatea (UPV/EHU) and Donostia International Physics Center (DIPC) — <sup>3</sup>IKERBASQUE, Basque Foundation for Science — <sup>4</sup>Max Planck Institute for Nuclear Physics, Heidelberg — <sup>5</sup>Astronomical Department of Physics and Astronomy, Aarhus University

Strong femtosecond laserfields can turn a helium nanodroplet into a highly charged nanoplasma. The initial ignition just needs a few electrons provided by tunnel ionization of helium or a dopant particle to start an avalanche of ionizations. The cluster is then completely within a few femtoseconds. Repulsion between ions leads to Coulomb explosion of the cluster and highly energetic ions and electrons are produced.

We use the velocity map imaging (VMI) technique to measure the energy and angular distribution of the electrons, and a time-of-flight (TOF) spectrometer to collect the ions. One helium droplet produces enough signal to measure VMI and TOF spectra for individual helium droplets hit by single laser pulses. With pump-probe measurements we investigate the time evolution of the system.

MO 14.2 Wed 14:15 K 2.016

**Highly Charged Rydberg Ions from the Coulomb Explosion of Clusters** — ●DZMITRY KOMAR, LEV KAZAK, MOHAMMED ALMASARANI, KARL-HEINZ MEIWEES-BROER, and JOSEF TIGGESBÄUMKER — Institut für Physik, Universität Rostock, 18059 Rostock, Germany

Ion emission from a nanoplasma produced in the interaction of intense optical laser pulses with argon clusters is studied resolving simultaneously charge states and recoil energies. By applying appropriate static electric fields we observe that a significant fraction of the ions Ar<sup>q+</sup> (q=1-7) have electrons with binding energies lower than 150 meV, i.e.

$n_{\text{Ryd}} \Rightarrow 15$  levels are populated. Charge state changes observed on a microsecond time scale can be attributed to electron emission due to autoionizing Rydberg states, indicating that high- $l$  Rydberg levels are populated as well. The experiments support theoretical predictions that a substantial fraction of delocalized electrons, which are bound with hundreds of eV to the nanoplasma after the laser exposure, fill up only meV bound ion states in the adiabatic expansion. We expect the process to be relevant for the long-term evolution of expanding laser-induced dense plasmas in general.

MO 14.3 Wed 14:30 K 2.016  
**Size Dependent Ion Yields from NaCl Nanoarticles Ionized by Intense Femtosecond Laser Pulses** — ●EGILL ANTONSSON, FELIX GERKE, LUCIA MERKEL, INA HALFPAP, BURKHARD LANGER, and ECKART RÜHL — Physical Chemistry, Freie Universität Berlin, D-14195 Berlin, Germany

Ionization of size selected nanoparticles by intense femtosecond laser pulses is studied by time-of-flight mass spectrometry. For NaCl nanoparticles ( $d=100-600$  nm), a size dependent modulation in the ratio of the yields of  $\text{Na}^+$  and  $\text{Cl}^+$  ions is observed, although the stoichiometry of the nanoparticles is constant irrespective of size. The observed size dependent ion yields are interpreted in terms of a model, where the intense laser pulses create a nanoplasma and the ion yields of the constituent elemental ions in the nanoparticles are determined by the plasma temperature and the ionization potentials of the elements.

MO 14.4 Wed 14:45 K 2.016  
**Size-dependent angular anisotropy in ion and electron emission of free NaCl nanoparticles excited by intense femtosecond laser pulses studied by Velocity Map Imaging spectroscopy** — ●FELIX GERKE, LUCIA MERKEL, EGILL ANTONSSON, and ECKART RÜHL — Physikalische Chemie, Freie Universität Berlin, Takustr. 3, 14195 Berlin

We present results regarding the angular distribution of ions and electrons emitted from NaCl nanoparticles ( $d = 100-500$  nm) during photoionization by intense femtosecond laser pulses obtained from Velocity Map Imaging (VMI) spectroscopy. The beam of a pulsed Ti:Sapphire laser ( $\lambda = 800$  nm,  $E = 1.55$  eV) is crossed in vacuum with a beam of free NaCl nanoparticles, that is focused by an aerodynamic lens, leading to ionization of the nanoparticles. Electrons and ions emitted from the nanoparticles are recorded by a VMI spectrometer. A size-dependent asymmetry in the electron and ion emission with respect to the propagation direction of the laser beam is observed. Here, more electron and ion emission is observed in the propagation direction of the laser pulses than in opposite direction. A comparison of electron and ion emission from nanoparticles of different size reveals the angular anisotropy, which is increasing with nanoparticle size. Furthermore, a comparison to model calculations simulating the internal electric field

of the nanoparticles by means of the discrete dipole approximation is used to attribute the experimentally observed angular anisotropy to size-dependent non-isotropic internal electric fields in the nanoparticles.

MO 14.5 Wed 15:00 K 2.016  
**Lasersheet nanoparticle imaging** — ●LENA WORBS<sup>1,2</sup>, AMIT SAMANTA<sup>1</sup>, DANIEL HORKE<sup>1,2</sup>, and JOCHEN KÜPPER<sup>1,2,3</sup> — <sup>1</sup>Center for Free-Electron Laser Science, DESY, Hamburg, Germany — <sup>2</sup>Center for Ultrafast Imaging, Universität Hamburg, Germany — <sup>3</sup>Department of Physics, Universität Hamburg, Germany

For coherent diffractive imaging of nanoparticles at free-electron lasers, sample delivery techniques and appropriate diagnostics have to be developed.

To characterize nanoparticle beams from aerodynamic cooling elements, e.g., aerodynamic lenses or buffer-gas cooling cells, a sheet of light is generated, and the scattered light of nanoparticles passing through the sheet is imaged with a microscope. Lasersheet imaging enables a full reconstruction of the transverse profile of the nanoparticle beam. Furthermore, it offers the opportunity to image the nanoparticle beam density without an additional setup, allowing the optimization of sample delivery methods.

MO 14.6 Wed 15:15 K 2.016  
**Cold and controlled nanoparticle beams for single particle diffractive imaging** — ●NILS ROTH<sup>1</sup>, SALAH AWEL<sup>1,2</sup>, AMIT SAMANTA<sup>1</sup>, ARMANDO ESTILLORE<sup>1</sup>, LENA WORBS<sup>1,2</sup>, MUHAMED AMIN<sup>1</sup>, KAROL DLUGOLECKI<sup>1</sup>, NICOLAI POHLMANN<sup>1</sup>, DANIEL HORKE<sup>1,2</sup>, and JOCHEN KÜPPER<sup>1,2,3,4</sup> — <sup>1</sup>Center for Free-Electron Laser Science, DESY, Hamburg, Germany — <sup>2</sup>Center for Ultrafast Imaging, Universität Hamburg, Germany — <sup>3</sup>Department of Physics, Universität Hamburg, Germany — <sup>4</sup>Department of Chemistry, Universität Hamburg, Germany

Coherent diffractive imaging at free-electron lasers promises to allow the reconstruction of the three-dimensional molecular structures of isolated particles at atomic resolution [1]. However, because of the typical low signal to noise ratio, this requires the collection of a large amount of diffraction patterns. Since every intercepted particle is destroyed by the intense x-ray pulse, a new and preferably identical sample particle has to be delivered into every pulse. Currently the inefficient delivery of particles and the correspondingly low number of strong diffraction patterns collected during typical beam times is one of the major limiting factors. With the aid of numerical simulations we developed new aerodynamic devices, such as aerodynamic lenses and buffer-gas cells, to produce cold and high-density beams of nanoparticles, e.g., viruses. We benchmark developed injectors in our aerosol beam characterisation setup, using novel laser-based particle detection schemes.

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

## MO 15: Complex Systems in the Gas Phase

Time: Wednesday 14:00–15:45

Location: PA 1.150

MO 15.1 Wed 14:00 PA 1.150  
**Two-dimensional electronic spectroscopy in the gas phase** — ●ULRICH BANGERT, LUKAS BRUDER, DANIEL UHL, MARCEL BINZ, MAX JAKOB, and FRANK STIENKEMEIER — Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg

Two-dimensional electronic spectroscopy (2DES) is a powerful tool to study complex dynamics in real time. Due to a lack of sensitivity, 2D spectroscopy has been almost exclusively applied to the condensed phase. However, an extension to the gas phase would provide valuable complementary information about the influence of environmental parameters (e.g. solvent molecules) and increase the dimensionality of 2D measurements by employing mass- and energy-resolved photoion/electron detection. To this end, we have built a 2DES setup based on quasi-continuous phase modulation combined with sensitive lock-in detection to facilitate 2DES of dilute molecular and cluster beams in the gas phase. We will present first results on dilute gas-phase systems combined with fluorescence and photoelectron detection, which confirm the high sensitivity of our setup and demonstrate the great potential in terms of resolution and versatility of this approach.

MO 15.2 Wed 14:15 PA 1.150

**Chirality investigated in the gas phase by two-color ionization** — ●ALEXANDER KASTNER, TOM RING, ROXANA SAVULEA, ARNE SENFTLEBEN, and THOMAS BAUMERT — Universität Kassel, Institut für Physik und CINSaT, 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 is known as photoelectron circular dichroism (PECD) [1, 2]. We observed highly structured asymmetries for resonance enhanced multi-photon ionization (REMPI) in the range of  $\pm 10\%$  on bicyclic Ketones [3, 4] and were able to study dependence on excitation wavelength [5].

Here we report on ionization of noble gas atoms as well as chiral molecules in the gas phase when mixing two colors (400/800 nm) in various relative and total intensity regimes. In the temporal overlap region, the superposition of two colors generates Lissajous-type electric field geometries driving electrons into trajectories not accessible by a single color field. The resulting momentum distributions unravel the imprint of field geometry on photoionization.

[1] I. Powis, *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)  
 [5] A. Kastner et al., J. Chem. Phys. 147, 013926, (2017)

MO 15.3 Wed 14:30 PA 1.150

**Excitation and ionization of atoms and molecules by vortex fields** — ●CARLOS MARIO GRANADOS-CASTRO and JAMAL BERAKDAR — Institut für Physik, Martin-Luther Universität Halle-Wittenberg, 06114 Halle (Saale)

The excitations of atoms and molecules with photons and charged particles is fairly well understood. The use of spatially structured beams such as vortex beams (VBs) of electrons or photons brings in new aspects related to the topology of VB, allowing to transfer a controllable amount of orbital angular momentum (OAM) to the sample. Ion trapping and optical tweezers are some of the applications of VBs. Also, it has been demonstrated that the access to the magnetic sublevels of atomic systems and the control of charge in spin-orbital coupled nanoscopic systems is possible with the use of OVs. Those applications are directly related with the emergence of new optical selection rules.

In this contribution we inspect the low energy electron emission and the excitations of atoms and molecules in vortex fields and present and analyze the modifications brought about by the topology of the exciting fields.

MO 15.4 Wed 14:45 PA 1.150

**IR/UV Ion-Dip-Spectroscopy of Reactive Species in the Gas Phase** — ●FLORIAN HIRSCH<sup>1</sup>, INGO FISCHER<sup>1</sup>, and ANOUK M. RIJS<sup>2</sup> — <sup>1</sup>Institute of Physical and Theoretical Chemistry, Wuerzburg University, Am Hubland Süd, 97074 Wuerzburg, Germany — <sup>2</sup>Institute for Molecules and Materials, Radboud University, FELIX Laboratory, Toernooiveld 7-c, 6525 ED Nijmegen, The Netherlands

Reactive species like radicals, carbenes and biradicals play an important role in a large variety of different chemical systems like combustion, atmospheric and interstellar chemistry. Due to their high reactivity regular analytic methods often cannot be applied and experiments must be performed in isolated environments.

Here we apply IR/UV Ion-Dip-Spectroscopy to investigate the structure of these reactive molecules and their reaction products in a free jet environment. This method combines mass selectivity of regular time-of-flight mass spectrometry with the structural information obtained by IR spectroscopy. Molecules are ionized in a [1+1] resonance enhanced multiphoton process at a fixed UV wavelength. Additionally, a free electron laser (Free Electron Laser for Infrared Experiments, FELIX, Nijmegen, Netherlands) scans the fingerprint region (550 - 1750 cm<sup>-1</sup>) resulting in mass selective IR spectra of the species in the molecular beam. Finally, comparison of the experimental data with calculations results in the structural data and may furthermore give insight into electronic structure and reaction pathways.

MO 15.5 Wed 15:00 PA 1.150

**Demystifying the azobenzene trans-cis isomerization process** — ●MARIO NIEBUHR, AXEL HEUER, and MARKUS GÜHR — Institute for Physics and Astronomy, Uni Potsdam, Germany

Azobenzene is a model system for photo-addressable switches both in chemistry and physics. The characteristic trans-cis isomerization, a fully reversible reorganization of the molecule's configuration under VIS/UV irradiation, is extensively used from addressable dyes to control systems for e.g. alignment of liquid crystal films in polarization switches. Albeit a decades long history of investigation and an inten-

sive theoretical discussion in the 2000s, fundamental questions about the exact process remain such as the mechanism (inversion, torsion, bond bending), the origin of the Kasha rule violation upon S2 excitation or a precise timeline.

We perform ultra-fast pump-probe spectroscopy on isolated azobenzene molecules in the gas phase, yielding time-resolved data free of environmental influences and therefore especially compatible with high-level ab-initio calculations. A commercial 100 kHz Yb:KGW system supplies ultra-short pulses from the NIR fundamental to UV harmonics, used for ion time-of-flight spectroscopy and soon transient absorption. First data will be presented and further planned experiments as well as their possible contribution to the azobenzene debate discussed, such as synchrotron UV excited fragmentation studies and pump-probe electron diffraction.

MO 15.6 Wed 15:15 PA 1.150

**Many-body resonances in dilute gas-phase systems** — ●LUKAS BRUDER<sup>1</sup>, MARCEL BINZ<sup>1</sup>, ULRICH BANGERT<sup>1</sup>, MARKUS SCHULZ-WEILING<sup>2</sup>, and FRANK STIENKEMEIER<sup>1</sup> — <sup>1</sup>Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg — <sup>2</sup>Department of Chemistry, University of British Columbia, Vancouver British Columbia, Canada V6T 1Z1

We investigate the collective behavior of atomic gases at low density and ambient temperature. In this regime, interatomic interactions are small and collective effects are masked by inhomogeneous broadening. Therefore, collective signatures are hard to detect with frequency domain methods. To this end, we have developed a highly efficient time-domain detection method based on a nonlinear femtosecond pump probe excitation scheme [1]. With this method, we detected, for the first time, four-body resonances in a rubidium vapor at densities down to 10<sup>8</sup> cm<sup>-3</sup>. Furthermore, we observe phase shifts in the absorption spectrum that are connected to the hyperfine levels of the system. Our findings are surprising considering the weak interparticle interaction present at the studied conditions, which has triggered some interest from theory to explain our results [2,3].

[1] L. Bruder, M. Binz, and F. Stienkemeier, Phys. Rev. A 92, 053412 (2015) [2] S. Mukamel, J. Chem. Phys. 145, 041102 (2016) [3] Z.-Z. Li, L. Bruder, F. Stienkemeier, and A. Eisfeld, Phys. Rev. A 95, 052509 (2017)

MO 15.7 Wed 15:30 PA 1.150

**Electronic Spectra of 1,2 Dimethoxybenzene in the Gas Phase** — ●CHRISTIAN HENRICHS, MARIE-LUISE HEBESTREIT, MICHAEL SCHNEIDER, and MICHAEL SCHMITT — Institute for Physical Chemistry I, Heinrich-Heine-University, Düsseldorf

The structural changes of 1,2 dimethoxybenzene upon excitation to the lowest electronically excited singlet state is interesting, since its two rotamers behave differently upon electronic excitation. We investigated these structural changes of 1,2 dimethoxybenzene using a combination of high resolution laser induced fluorescence spectroscopy (HRLIF) and vibrationally resolved fluorescence emission spectroscopy. The HRLIF spectra yield the rotational constants of the ground and in the first excited state, which are not sufficient for a complete structural determination. The problem of fitting structural changes of 3N-6 geometry parameters to a set of only 3 rotational constants can be resolved using additional information from complementary experiments. With the aid of Franck-Condon (FC) analyses using a normal mode analysis based on the CC2/cc-pVTZ optimized structures we were able to fit the relevant parameters both to the FC intensities as well as to the rotational constants.

## MO 16: Molecules in Intense Laser Fields (joint session MO/A)

Time: Wednesday 14:00–15:45

Location: PA 2.150

MO 16.1 Wed 14:00 PA 2.150

**Strong-field ionization of laser-aligned molecules** — ●JOCHEN KÜPPER — Center for Free-Electron Laser Science, DESY, Hamburg — Center for Ultrafast Imaging, Universität Hamburg — Department of Physics and Department of Chemistry, Universität Hamburg

The interaction of strong laser fields with matter intrinsically enables the imaging of transient dynamics with extremely high spatiotemporal resolution. This paradigm of photophysics has grown into new emerging research areas, ranging from attosecond science to laser-induced

electron diffraction, providing new insight into atoms, molecules and, more recently, condensed matter. Also, the earliest moments of strong-field interactions have attracted attention for capturing the intrinsic nature of strong-field physics. While pioneering attosecond science experiments and molecular-frame measurements revealed non-trivial spatiotemporal features in electron tunneling, these initial conditions are generally considered a weak perturbation. We investigated strong-field ionization in the molecular frame. Carbonyl sulfide (OCS) molecules were quantum-state selected, strongly laser aligned, and ionized using short near-infrared laser pulses. We analyzed the dynamics of the elec-

tron and discuss the obtained molecular-frame photoelectron-angular distributions. Our findings have strong impact in the interpretation of laser induced electron diffraction, where the photoelectron momentum distribution is used to retrieve molecular structures. Furthermore, the encoding of the time-energy relation in the photoelectron momenta provides new ways of probing electron tunneling and the molecular potential with sub-femtosecond resolution.

MO 16.2 Wed 14:30 PA 2.150

**Intermolecular vibration in (NO<sub>2</sub>)<sub>2</sub> molecules studied with few-cycle laser pulses** — KATRIN REININGER, JINGMING LONG, FEDERICO FURCH, MARC J.J. VRAKKING, ●CLAUS P. SCHULZ, and JOCHEN MIKOSCH — Max-Born-Institut, Max-Born-Str. 2a, 12489 Berlin, Germany

The intermolecular vibration of the NO<sub>2</sub> dimer molecule is an interesting object of study for high-harmonic generation and strong-field ionization probes of molecular dynamics [1]. The vibration can be conveniently excited by impulsive stimulated Raman scattering (ISRS).

Here we measure the amplitude of the intramolecular motion using photofragment kinetic energy spectroscopy. We employ a newly developed high repetition rate Optical Parametric Chirped-Pulse Amplification (OPCPA) laser system delivering sub-7 fs duration pulses [2] in combination with a novel velocity map imaging (VMI) spectrometer based on an in-vacuum pixel detector [3].

Following ISRS, the molecule is strong-field ionized to the (NO<sub>2</sub>)<sub>2</sub><sup>+</sup> A<sub>g</sub> state and undergoes dissociation. We observe an oscillation in the kinetic energy release of NO<sub>2</sub><sup>+</sup> with pump-probe delay on the 130fs time-scale of the O<sub>2</sub>N–NO<sub>2</sub> vibration. From the kinetic energy spectrum and the calculated potential surfaces, we determine the amplitude of the vibrational motion in the (NO<sub>2</sub>)<sub>2</sub> ground state.

[1] W. Li, *et al.*, Science 322, 1207 (2008).

[2] F. J. Furch, *et al.*, Opt. Express 24, 19293 (2016).

[3] J. M. Long, *et al.*, J. Chem. Phys. 147, 10, 013919 (2017).

MO 16.3 Wed 14:45 PA 2.150

**Intensity dependence of Photon Energy Sharing in H<sub>2</sub> Multi-photon Ionization** — ●PATRICK FROSS, DENHI MARTINEZ, NICOLAS CAMUS, THOMAS PFEIFER, and ROBERT MOSHAMMER — Max-Planck-Institut für Kernphysik, Heidelberg, Germany

When ionizing molecules with strong laser fields, the dynamics of photofragmentation determines how the photon energy is shared between the resulting fragments. Understanding this photon energy sharing helps to understand and eventually control the fragmentation process in intense laser fields. Recently Joint-Energy-Spectra (JES) have been observed for dissociative and double ionization of H<sub>2</sub> in order to investigate photon-number-resolved ionization dynamics at laser intensities of  $5 \cdot 10^{13}$ – $1 \cdot 10^{14}$  W/cm<sup>2</sup>. We present measurements of full 3D photon-number-resolved momentum distributions in H<sub>2</sub> dissociative and double ionization for different intensities using 35fs laser pulses with a central wavelength of 395nm and recording the reaction fragments with a Reaction Microscope. The JES clearly shows that for high laser intensities events involving different numbers of photons cannot be distinguished anymore.

MO 16.4 Wed 15:00 PA 2.150

**Fragmentation dynamics of HeH<sup>+</sup> in intense ultrashort laser pulses** — ●PHILIPP WUSTELT<sup>1,2</sup>, FLORIAN OPPERMAN<sup>3</sup>, LUN YUE<sup>4</sup>, MAX MÖLLER<sup>1,2</sup>, A. MAX SAYLER<sup>1,2</sup>, MANFRED LEIN<sup>3</sup>, STEFANIE GRÄFE<sup>4</sup>, and GERHARD G. PAULUS<sup>1,2</sup> — <sup>1</sup>Institute of Optics and Quantum Electronics, Friedrich-Schiller-University Jena, D-

07743 Jena, Germany — <sup>2</sup>Helmholtz Institute Jena, D-07743 Jena, Germany — <sup>3</sup>Institut für Theoretische Physik, Leibniz Universität Hannover, Appelstraße 2, 30167 Hannover — <sup>4</sup>Institute of Physical Chemistry, Friedrich-Schiller University-Jena, Helmholtzweg 4, D-07743 Jena, Germany

The helium hydride molecular ion, HeH<sup>+</sup>, is the simplest heteronuclear polar molecule and serves as a benchmark system for the investigation of multi-electron molecules and molecules with a permanent dipole. We specifically address the question: How does the permanent dipole of HeH<sup>+</sup> affect the fragmentation dynamics in intense ultrashort laser pulses? We study the laser induced laser-induced fragmentation; including non-ionizing dissociation, single ionization and double ionization; of an ion beam of helium hydride and an isotopologue at various wavelengths and intensities. These results are interpreted using reduced dimensionality solutions to the time-dependent Schrödinger equation and with simulations based on Dressed surface hopping.

MO 16.5 Wed 15:15 PA 2.150

**Electron-Nuclear Coupling through Autoionizing Rydberg States after Strong-field Excitation of Molecules** — ●YONGHAO MI, NICOLAS CAMU, LUTZ FECHNER, MARTIN LAUX, ROBERT MOSHAMMER, and THOMAS PFEIFER — Max-Planck-Institute for Nuclear Physics

Channel-selective electron emission from strong-field photo-ionization of H<sub>2</sub> 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 (H<sub>2</sub><sup>+</sup>) 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 neutral H<sub>2</sub> molecules in which vibrational energy is transferred to electronic energy. This general mechanism, provides access to the excited-state population of molecular ions produced in a strong-field interaction.

MO 16.6 Wed 15:30 PA 2.150

**Probing electronic structure via molecular-frame photoelectron imaging** — ●JOSS WIESE<sup>1</sup>, SEBASTIAN TRIPPEL<sup>1</sup>, and JOCHEN KÜPPER<sup>1,2,3</sup> — <sup>1</sup>Center for Free-Electron Laser Science, DESY, Hamburg — <sup>2</sup>The Hamburg Center for Ultrafast Imaging, Hamburg — <sup>3</sup>Department of Physics, University of Hamburg

Chemical function arises from the interplay of valence electrons and a view at the evolution of the highest occupied molecular orbitals (HOMOs) during a chemical reaction promises direct insight into the fundamentals of chemistry. For this purpose we employ tomographic photoelectron imaging [1] of spatially confined ensembles of indole strong-field ionized by intense near-infrared laser pulses. Reconstructed static three-dimensional photoelectron distributions in molecular-frame momentum space (MF-ARPES) will be presented. These exhibit distinct manifestations of tunneling as well as multiphoton ionization, which allow for the mapping of the molecule's electronic structure. The technique yields experimental access to properties of the HOMO potential energy surface that are commonly only approachable through quantum chemistry. Based on the measured photoelectron distributions the importance of resonant electronic states for the tunneling ionization pathway will be enquired and the validity of molecular strong-field ionization models will be tested.

[1] Maurer, Dimitrovski, Christensen, Madsen, Stapelfeldt, *Phys. Rev. Lett.* **109**, 123001 (2012)

## MO 17: Posters 2: Cold Molecules and Clusters

Time: Wednesday 16:15–18:15

Location: Orangerie

MO 17.1 Wed 16:15 Orangerie

**A high density source of cold, slow and rotationally pure polar molecules** — ●MANUEL KOLLER, THOMAS GANTNER, XING WU Ø, MARTIN ZEPPENFELD, SOTIR CHERVENKOV, and GERHARD REMPE — Max-Planck-Institut für Quantenoptik, Garching 85748, Germany

Cold polar molecules provide fascinating research possibilities in physics and chemistry. However, densities of cold and slow molecules, achieved in past experiments have been insufficient for many applications. By combining cryogenic buffer gas cooling and centrifuge decel-

eration we put an end to this problem. Our source delivers a record high flux exceeding  $10^{10}$ s<sup>-1</sup> and densities up to  $10^9$ cm<sup>-3</sup> of internally cold polar molecules with a single state purity of up to 92% [1] at kinetic energies corresponding to less than 1K [2]. The generality of our method makes it applicable to a wide range of molecular species (ND<sub>3</sub>, CH<sub>3</sub>F, CHF<sub>3</sub>, etc.). Beside enabling detailed collision studies our technique could serve as an ideal source for optoelectrical Sisyphus cooling and testing fundamental physics.

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



[2] X. Wu et al., *Science* 2017, 358, 645-648

ø Current address: Department of Physics, Yale University, New Haven, CT 06511, USA; Department of Physics, Harvard University, Cambridge, MA 02138, USA

MO 17.2 Wed 16:15 Orangerie

**A Molecular Zeeman slowing scheme** — ●PAUL KAEBERT, NIKLAS REINHARDT, MAURICE PETZOLD, PHILIPP GERSEMA, MIRCO SIERCKE, and SILKE OSPELKAUS — Institut für Quantenoptik

We report on our progress in implementing a novel scheme for slowing laser-coolable, buffer-gas cooled molecules, reminiscent of Zeeman slowing. We show the results of our proof of principle experiment, realizing the scheme on the D1-line of  $^{39}\text{K}$ , and detail our progress on performing the experiment on molecules. From our theoretical simulations and our experimental results we expect the technique to outperform current slowing methods, and hope that the resulting large flux of trappable molecules will be the enhancement needed to produce large, ultra-cold ensembles of directly cooled molecules.

MO 17.3 Wed 16:15 Orangerie

**Generation of charged water clusters for hybrid trap experiments** — ●JAN TRAUTMANN<sup>1</sup>, NINA BEIER<sup>1</sup>, HENRY LOPEZ<sup>1</sup>, JONAS TAUCH<sup>1</sup>, BASTIAN HOLKEMEIER<sup>1</sup>, ROLAND WESTER<sup>2</sup>, and MATTHIAS WEIDEMÜLLER<sup>1,3</sup> — <sup>1</sup>Physikalisches Institut, Universität Heidelberg, Im Neuenheimer Feld 226, 69120 Heidelberg, Germany — <sup>2</sup>Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck, Technikerstraße 25/3, A-6020 Innsbruck, Austria — <sup>3</sup>University of Science and Technology of China, Shanghai Branch, Shanghai 201315, China

We present a novel design of a pulsed plasma discharge ion source for the creation of a vast variety of anions, especially hydrated water clusters. The ions are produced inside a glow discharge plasma and characterised via a Wiley-McLaren mass spectrometer. We report the successful creation of different species of anions from various gas compositions. In future experiments, the water clusters ions will be stored in a hybrid atom-ion trap for studies of chemical reactions at ultralow temperatures.

MO 17.4 Wed 16:15 Orangerie

**Laser induced fluorescence detection of ultracold formaldehyde** — ●MARTIN IBRÜGGER, ALEXANDER PREHN, MAXIMILIAN LÖW, MARTIN ZEPPENFELD, and GERHARD REMPE — Max-Planck-Institut für Quantenoptik, Hans-Kopfermann-Str. 1, 85748 Garching

Ultracold molecules offer ideal perspectives for a variety of exciting applications. Proposed experiments range from the investigation of ultracold chemistry over quantum simulation to high-precision spectroscopy. Optoelectrical Sisyphus cooling has proven to be capable to provide a sizeable number of  $3 \cdot 10^5$  molecules of formaldehyde ( $\text{H}_2\text{CO}$ ) at temperatures below 1 mK [1]. However, in the past the experiment has suffered from a low detection efficiency of the quadrupole mass spectrometer employed for counting the molecules, thus severely increasing measurement times.

Here, we present a scheme for continuous detection of formaldehyde based on laser induced fluorescence (LIF). Molecules are electronically excited by a UV-laser and successively fluoresce. No cycling transition is available due to bad Franck-Condon overlap and thus light collection optics covering a large solid angle is mandatory. We present techniques to reduce stray light by many orders of magnitude in order to allow for a high signal to noise ratio. This setup should enable detection of formaldehyde with a sensitivity increased by about a factor of 30 and thus bring many of the proposed applications within reach and open up the way for fascinating new experiments.

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

MO 17.5 Wed 16:15 Orangerie

**Towards Direct Laser Cooling of Barium Monofluoride** — ●TOBIAS SIXT, LUCAS HOFER, ANNA GRIBBON, TOBIAS REINSCH, RALF ALBRECHT, and TIM LANGEN — 5. Physikalisches Institut and Center for Integrated Quantum Science and Technology (IQST), Universität Stuttgart, Germany

We present a new experimental setup for the laser cooling and trapping of barium monofluoride molecules. Laser cooling of molecules had long been considered impossible due to their complex vibrational and rotational level structure. However, beneficial Franck-Condon factors and selection rules allow for optical cycling in many molecular species, including barium monofluoride. The molecules will be generated through laser ablation in cryostat and precooled by collisions with a 4K he-

lium buffer gas. This results in a cold and intense beam that provides ideal starting conditions for transversal laser cooling, laser slowing and subsequent loading of a 3D magneto-optical trap. The resulting cold molecular gas will pave the way for a large number of novel and interdisciplinary applications ranging from few- and many-body physics to cold chemistry and tests of fundamental symmetries.

MO 17.6 Wed 16:15 Orangerie

**Near threshold photodetachment spectroscopy of  $\text{CN}^-$  and  $\text{C}_3\text{N}^-$  in a cryogenic multipole trap** — MALCOLM SIMPSON<sup>1</sup>, ●MARKUS NÖTZOLD<sup>1</sup>, ALICE SCHMIDT-MAY<sup>1</sup>, ROBERT WILD<sup>1</sup>, VIATCHESLAV KOKOULINE<sup>2</sup>, and ROLAND WESTER<sup>1</sup> — <sup>1</sup>Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck, A-6020, Innsbruck (Austria) — <sup>2</sup>Department of Physics University of Central Florida Orlando, FL 32816, USA

Molecular anions often exist only in a single bound electronic state. However, neutral molecules with a permanent dipole moment greater than the critical value of 1.625 D interacting with a single electron are expected to possess additional weakly bound states close to the detachment threshold (dipole bound states)[1] and metastable resonance states in the continuum (dipole scattering states) [2]. Using a cryogenic 22-pole trap we are able to probe anionic cyanides, study their interaction with light and search for evidence of dipole bound states. Current experiments of near-threshold photodetachment of the  $\text{C}_3\text{N}^-$  ( $\mu \sim 3.6$  D) anion and the  $\text{CN}^-$  ( $\mu \sim 1.4$  D) anion are presented and future prospects are given.

[1] Carelli, F.; Gianturco, F. A.; Wester, R.; Satta, M., *J. Chem. Phys.* **141** (2014) 054302.

[2] Carelli, F.; Satta, M.; Grassi, T.; Gianturco, F. A., *Astrophys. J.* **774** (2013) 97.

MO 17.7 Wed 16:15 Orangerie

**Towards reaction studies of  $\text{CN}^-$  with atomic hydrogen in a cryogenic multipole trap** — ●ELIN CARAPOVIC, ROBERT WILD, MALCOLM SIMPSON, ALICE SCHMIDT-MAY, MARKUS NÖTZOLD, and ROLAND WESTER — Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck, A-6020 Innsbruck, Austria

After the radioastronomical discovery of the first interstellar anions, interest has grown in understanding the formation and destruction pathways of negative ions in the interstellar medium. Our group has previously performed photodetachment studies on  $\text{C}_n\text{H}^-$  [1],  $\text{CN}^-$  and  $\text{C}_3\text{N}^-$  anions [2], but reactions with hydrogen may also play a significant role. Reaction rate studies of  $\text{C}_n\text{H}^-$  with molecular hydrogen show vanishing rates [3]. Here we focus on the role of atomic hydrogen in reactions with interstellar anions. Our 22-pole cryogenic ion trap is a versatile tool to simulate interstellar conditions, and we have incorporated a hydrogen atom source into our system. This allows us to study the reaction rates of  $\text{CN}^-$  with atomic hydrogen at cold temperatures.

[1] T. Best, R. Otto, S. Trippel, P. Hlavenka, A. von Zastrow, S. Eisenbach, S. Jézouin, R. Wester, E. Vigren, M. Hamberg, *Astrophys. J.* **742**, (2011).

[2] S. S. Kumar, D. Hauser, R. Jindra, T. Best, Š. Roučka, W. D. Geppert, T. J. Millar, and R. Wester, *Astrophys. J.* **776**, (2013).

[3] E. S. Endres, O. Lakhmanskaya, D. Hauser, S. E. Huber, T. Best, S. S. Kumar, M. Probst, and R. Wester, *J. Phys. Chem. A*, **118**, (2014).

MO 17.8 Wed 16:15 Orangerie

**Sensitive Search for an EDM on the Electron using BaF Molecules** — ●THOMAS MEIJKNECHT<sup>1</sup>, PARUL AGGARWAL<sup>1</sup>, HENDRICK L. BETHLEM<sup>2</sup>, ANASTASIA BORSHEVSKY<sup>1</sup>, KEVIN ESAJAS<sup>1</sup>, PI HAASE<sup>1</sup>, STEVEN HOEKSTRA<sup>1</sup>, KLAUS JUNGSMANN<sup>1</sup>, MAARTEN MOOIJ<sup>2</sup>, ROB TIMMERMANS<sup>1</sup>, WIM UBACHS<sup>2</sup>, LORENZ WILLMANN<sup>1</sup>, and ARTEM ZAPARA<sup>1</sup> — <sup>1</sup>Van Swinderen Institute, University of Groningen, NL, and Nikhef, NL — <sup>2</sup>LaserLab, Department of Physics and Astronomy, Vrije Universiteit Amsterdam, NL

The observation of an electron electric dipole moment (eEDM) larger than the value allowed by the Standard Model (SM) of particle physics would be direct evidence of new physics. An upper limit of the eEDM constrains extensions to the SM. The barium monofluoride molecule (BaF) is an excellent system for electron EDM searches. Its structure gives rise to a large effective electric field  $\vec{E}_{\text{eff}}$  experienced by the valence electron, if the molecules are polarized by an external electric field. The particular structure of BaF enables their slowing down in a Stark decelerator [1] to velocities of several 10 m/s. With the addition of laser cooling a bright and slow molecular beam can be created.



The components of the experiment, from the cryogenic source of BaF to the magnetically shielded interaction zone will be discussed and the experimental strategy will be explained. The goal of the project is a statistical limit of  $5 \cdot 10^{-30}$  *ecm*. At the projected precision the results of this experiment complement results in high energy physics experiments, e.g. at LHC.

[1] J.E. van den Berg, et al., *J. Mol. Spec.* 300, 22 (2014)

MO 17.9 Wed 16:15 Orangerie

**Cryo IR Spectroscopy of N<sub>2</sub> and H<sub>2</sub> on Ru<sub>8</sub><sup>+</sup>** — SEBASTIAN DILLINGER<sup>1</sup>, MATTHIAS P. KLEIN<sup>1</sup>, ANNIKA STEINER<sup>1</sup>, DAVID C. McDONALD II<sup>2</sup>, MICHAEL A. DUNCAN<sup>2</sup>, MANFRED M. KAPPES<sup>3</sup>, and GERON NIEDNER-SCHATTEBURG<sup>1</sup> — <sup>1</sup>Fachbereich Chemie and Forschungszentrum OPTIMAS, Technische Universität Kaiserslautern, 67663 Kaiserslautern, Germany — <sup>2</sup>Department of Chemistry, University of Georgia, Athens, Georgia 30602, USA — <sup>3</sup>Institute of Physical Chemistry, Karlsruhe Institute of Technology (KIT), Fritz-Haber-Weg 2, 76131 Karlsruhe, Germany

We present the cryo IR spectra of [Ru<sub>8</sub>(H<sub>2</sub>)<sub>l</sub>]<sup>+</sup> l = 1 - 8, [Ru<sub>8</sub>(N<sub>2</sub>)<sub>m</sub>]<sup>+</sup> m = 1 - 8, and the coadsorbed [Ru<sub>8</sub>(H<sub>2</sub>)<sub>1</sub>(N<sub>2</sub>)<sub>4</sub>]<sup>+</sup> and [Ru<sub>8</sub>(N<sub>2</sub>)<sub>4</sub>(H<sub>2</sub>)<sub>1</sub>]<sup>+</sup> species in isolation. The [Ru<sub>8</sub>(H<sub>2</sub>)<sub>l</sub>]<sup>+</sup> species with l > 1 reveal bands in the region of 1800 cm<sup>-1</sup> to 1880 cm<sup>-1</sup>, which are a strong evidence for the formation of a hydride species. The [Ru<sub>8</sub>(N<sub>2</sub>)<sub>m</sub>]<sup>+</sup> species reveal features redshifted to the free N<sub>2</sub> vibration (2300 cm<sup>-1</sup>) in the region of 2190 to 2300 cm<sup>-1</sup>, which are attributed to the vibration of head on adsorbed N<sub>2</sub>. The H<sub>2</sub>-N<sub>2</sub>-coadsorbates [Ru<sub>8</sub>(H<sub>2</sub>)<sub>1</sub>(N<sub>2</sub>)<sub>4</sub>]<sup>+</sup> and [Ru<sub>8</sub>(N<sub>2</sub>)<sub>4</sub>(H<sub>2</sub>)<sub>1</sub>]<sup>+</sup> species reveal spectral differences in the hydride region of the IR spectra. We interpret these differences to different positioning of the hydrides on the Ru cluster. This positioning is influenced by the sequence of adsorption (first H<sub>2</sub> and then N<sub>2</sub> or first N<sub>2</sub> and then H<sub>2</sub>) and the possibility of migration of the hydrides on the Ru<sub>8</sub><sup>+</sup> cluster.

MO 17.10 Wed 16:15 Orangerie

**Collinear TOF electron impact for detecting high masses in cluster beam** — AUDREY SCOGNAMIGLIO, ALEXANDER RUF, KATRIN DULITZ, BERND VON ISSENDORFF, and FRANK STIENKEMEIER — Physikalisches Institut, Universität Freiburg, Germany

The isolation of atoms, molecules and molecular complexes in rare cluster beams, and particularly in helium nanodroplets, offers a versatile method for the study of energetic and dynamical properties of these systems, because it provides low-temperature conditions with minimal perturbation by the environment. For the detection and mass selection of the needed high mass range, as well as to give insights into the mass and charge distribution, it is advantageous to use a combination of electron impact ionization, photo-ionization and time-of-flight (TOF) spectrometry in a collinear arrangement to the cluster beam. We combined an electron gun with a TOF spectrometer in order to provide a versatile ionization method and a good mass resolution. In this presentation, the characterization of the setup and first results using doped helium nanodroplets and rare gas clusters will be discussed.

MO 17.11 Wed 16:15 Orangerie

**Setup for production and characterization of molecular clusters from liquids** — JOHANNES VIEHMANN, PHILIP WENZEL, ANDREAS HANS, REBECCA SCHAF, ARNO EHRESMANN, and ANDRÉ KNIE — Institut für Physik and Center for Interdisciplinary Nanostructure Science and Technology (CINSA<sub>T</sub>), Universität Kassel, Heinrich-Plett-Straße 40, 34132 Kassel, Germany

In order to investigate real life processes within aqueous environments it is necessary to reconstruct natural systems of interest under laboratory conditions. Supersonic expansion is commonly used for the production of molecular clusters. Here we show how mass spectrometry enables us to adequately determine cluster sizes and characterize the parameter room of a cluster source. A setup for production and characterization of molecular clusters from liquids using a two chamber cluster source with integrated heating system is described.

MO 17.12 Wed 16:15 Orangerie

**Production and analysis of micro-solvated organic molecules** — REBECCA SCHAF, JOHANNES VIEHMANN, PHILIP WENZEL, ANDREAS HANS, ARNO EHRESMANN, and ANDRÉ KNIE — Institut für Physik, Universität Kassel, Heinrich-Plett-Straße 40, 34132 Kassel, Germany

The preparation of water clusters doped with organic molecules is a suited method for the experimental exploration of the behaviour of

such molecules in natural (aqueous) environments. Here, we present a versatile cluster source for the production of water clusters doped with organic liquids and low-melting solids. Among others, the source enables investigations on mixing ratio effects, isotope effects, and temperature dependencies. We describe the principle of this two-chamber cluster source and present first experimental data.

MO 17.13 Wed 16:15 Orangerie

**Mass Selected Water Clusters and Solvated Ions for X-Ray Spectroscopy - First Results** — JULIUS SCHWARZ, IVAN BAEV, FRIDTJOF KIELGAST, and MICHAEL MARTINS — Institute for Experimental Physics, University Hamburg, Germany

A characterization of the geometric and electronic structure of ionized water clusters and solvated ions is crucial for a detailed understanding of Ionic Solvation and its effects on the reactivity of the solute. Such a characterization can be obtained by studying ionized water clusters and solvated ions in the gas phase using X-Ray spectroscopy. The challenge of supplying an ionized cluster beam can be solved by injecting water molecules into the flowing afterglow regime of Argon plasma to enable formation of the ionized water clusters. The same technique can be used to supply a variety of solvated ions.

Here, we present first results on commissioning a Flowing Afterglow Ion Source to supply mass-selected water clusters and solvated ions to the Photon Ion Spectrometer at PETRA III (PIPE) in Hamburg for characterization by X-Ray spectroscopy. We will report on source design, the flowing afterglow technique, mass spectra of the ion beam, as well as ion current after mass selection.

MO 17.14 Wed 16:15 Orangerie

**Molecular Frame Angular Emission Distributions of Resonant ICD Electrons in Ne<sub>2</sub> and HeNe** — ABIR MHAMDI<sup>1</sup>, FLORIAN TRINTER<sup>2</sup>, TILL JAHNKE<sup>2</sup>, KIRILL GOKHBERG<sup>3</sup>, REINHARD DÖRNER<sup>2</sup>, and PHILIPP V. DEMEKHIN<sup>1</sup> — <sup>1</sup>Institut für Physik und CINSA<sub>T</sub>, Universität Kassel, 34132 Kassel, Germany — <sup>2</sup>Institut für Kernphysik, Universität Frankfurt, 60438 Frankfurt am Main, Germany — <sup>3</sup>Theoretische Chemie, Universität Heidelberg, Im Neuenheimer Feld, 69120 Heidelberg, Germany

Molecular Frame Angular Distributions (MFADs) of slow electrons released by Interatomic Coulombic Decay in van der Waals dimers are studied by the Single Center (SC) method [1] including the underlying nuclear dynamics. Specifically, we considered the spectator resonant ICD after 2s - np inner valence excitation of Ne dimers, which is the dominant decay pathway for n ≥ 5 [2]. In addition, we investigated the photoionization of HeNe across the He(1s3p) excitation which is a good candidate for the antenna-receiver mechanism [3]. Theoretical predictions for HeNe are in good agreement with the results of the coincidence experiments carried out by COLTRIMS technique [4]. It is demonstrated that MFAD of the resonant ICD electrons provides a direct access to the symmetry of the intermediate electronic states.

References: [1] Ph. V. Demekhin, et al., *Journal of Chemical Physics* **134**, 024113 (2011). [2] S. Kopelke, et al., *J. Chem. Phys.* **130**, 144103 (2009). [3] F. Trinter, et al., *Phys. Rev. Lett.* **111**, 093401 (2013). [4] R. Dörner, et al., *Physics Reports* **330**, 95 (2000).

MO 17.15 Wed 16:15 Orangerie

**Investigation of the geometric and electronic structure of nitrogen clusters** — HUDA OTTO, DANA BLOSS, ANDREAS HANS, XAVER HOLZAPFEL, CATMARN KÜSTNER-WETEKAM, MAIK MOROWSKI, CHRISTIAN OZGA, PHILIPP SCHMIDT, ARNO EHRESMANN, and ANDRÉ KNIE — Institut für Physik and Center for Interdisciplinary Nanostructure Science and Technology (CINSA<sub>T</sub>), Universität Kassel, Heinrich-Plett-Straße 40, 34132 Kassel, Germany

Lately, evidence for an Intermolecular Coulombic Decay (ICD) in nitrogen van-der-Waals-dimers has been found and ICD has been suggested to widely occur in biologic tissues. While the electronic states of gaseous nitrogen have been subject of scientific investigations for decades, the geometric and electronic structure of clusters are not yet completely understood. N<sub>2</sub>-clusters have recently been in discussion because of a showcase, which might be a candidate for future medical applications of ICD [1, 2]. In order to investigate the ICD in N<sub>2</sub>-clusters in detail, it is necessary to know their electronic structure. Photon-induced fluorescence spectroscopy delivers information about the electronic states of a species. To contribute to the above-mentioned discussion fluorescence spectroscopy is introduced as a technique for investigating the geometric and electronic structure of nitrogen clusters and first data are presented.

- [1] Trinter et al., Nature **505** 664 (2014)  
 [2] Gokhberg et al., Nature **505** 661 (2014)

MO 17.16 Wed 16:15 Orangerie

**Theory of photoassociation processes of alkali metal clusters** — ●JAN SCHNABEL<sup>1,2</sup> and ANDREAS KÖHN<sup>1,2</sup> — <sup>1</sup>Institut für Theoretische Chemie, Universität Stuttgart — <sup>2</sup>Center for Integrated Quantum Science and Technology

Understanding molecular binding mechanisms on a fundamental level and creating molecules in exactly defined quantum states are major goals in the growing area of ultracold chemistry. An important method to produce ultracold molecules is photoassociation which has been demonstrated for Rb dimers in [1,2]. At the same time an experimental realization of higher associated clusters succeeded so far only with alkali metal atoms formed on helium droplets [3]. An encouraging approach for preparing isolated Rb<sub>3</sub> combines photoassociation with cavity QED allowing for non-destructive detection of ultracold molecules.

We use *ab-initio* calculations to investigate possible states, transitions and spin-orbit couplings to propose a realistic photoassociation scheme for realizing spin-polarized Rb<sub>3</sub> clusters. To this end we construct potential energy surfaces of excited states applying a general interpolation method within the framework of RKHS (reproducing kernel Hilbert space) theory. Moreover we analyze long-range interactions between Rb<sub>2</sub> and Rb as well as the vibrational levels of some trimer states.

- [1] J. Hecker Denschlag, Phys. Rev. A **82**, 052514 (2010)  
 [2] J. Hecker Denschlag, Phys. Rev. A **95**, 062507 (2017)  
 [3] W.E. Ernst, J. Chem. Phys. **45**, 114501 (2008)

MO 17.17 Wed 16:15 Orangerie

**3D high resolution diffractive imaging of individual silver clusters** — ●J. JORDAN<sup>1</sup>, B. LANGBEHN<sup>1</sup>, A. ULMER<sup>1</sup>, J. ZIMMERMANN<sup>5,1</sup>, S. DOLD<sup>2</sup>, B. v. ISSENDORFF<sup>2</sup>, I. BARKE<sup>3</sup>, H. HARTMANN<sup>3</sup>, F. MARTINEZ<sup>3</sup>, K. OLDENBURG<sup>3</sup>, K. MEIWES-BROER<sup>3</sup>, T. FENNEL<sup>3</sup>, C. BOMME<sup>4</sup>, J. CORREA<sup>4</sup>, S. DÜSTERER<sup>4</sup>, B. ERK<sup>4</sup>, B. MANSCHWETUS<sup>4</sup>, R. TREUSCH<sup>4</sup>, T. MÖLLER<sup>1</sup>, and D. RUPP<sup>1,5</sup> — <sup>1</sup>TU Berlin — <sup>2</sup>U. Freiburg — <sup>3</sup>U. Rostock — <sup>4</sup>FLASH@DESY — <sup>5</sup>MBI Berlin

Short-wavelength free-electron lasers (FELs) have opened a window into the nano cosmos. Their high intensity and short pulse duration allow capturing of high resolution "snapshots" of single nanometer-sized objects in free flight. Single silver clusters, created by a magnetron sputter source in a broad size distribution, were imaged in a diffraction before destruction approach using extreme ultraviolet (XUV) and soft x-ray pulses from the FEL in Hamburg (FLASH). In a previous work, a large variety of structural motifs were identified by using wide angle diffraction [Barke *et al.*, Nat. Comm. **6** (2015)]. There, the scattering signal at large angles, which contains 3D information on particle shape and orientation, was recorded in the XUV regime. However, the use of long wavelengths decreases spatial resolution. In this work, scattering images obtained at 5 nm and 13.6 nm were compared to test whether 3D information can be reliably extracted at short wavelengths while maintaining high resolution. This is key to time resolved imaging studies on light-induced electronic excitation and ultrafast melting of metal

clusters, which will be further explored in an upcoming experiment.

MO 17.18 Wed 16:15 Orangerie

**Ionization dynamics of methane clusters** — ●A. HEILRATH<sup>1</sup>, M. SAUPPE<sup>1</sup>, K. KOLATZKI<sup>1,2</sup>, B. LANGBEHN<sup>1</sup>, B. SENFFTLIEBEN<sup>1</sup>, A. ULMER<sup>1</sup>, J. ZIMMERMANN<sup>1,2</sup>, L. FLÜCKIGER<sup>3</sup>, T. GORKHOVER<sup>1,4</sup>, C. BOSTEDT<sup>5,6</sup>, Y. KUMAGAI<sup>5</sup>, C. BOMME<sup>7</sup>, S. DÜSTERER<sup>7</sup>, B. ERK<sup>7</sup>, M. KUHLMANN<sup>7</sup>, C. PASSOW<sup>7</sup>, D. ROLLES<sup>7,8</sup>, D. ROMPOTIS<sup>7</sup>, S. TOLEIKIS<sup>7</sup>, R. TREUSCH<sup>7</sup>, T. FEIGL<sup>9</sup>, T. MÖLLER<sup>1</sup>, and D. RUPP<sup>1,2</sup> — <sup>1</sup>TU Berlin — <sup>2</sup>MBI Berlin — <sup>3</sup>La Trobe University, Melbourne, Australia — <sup>4</sup>SLAC Menlo Park, USA — <sup>5</sup>Argonne National Lab, USA — <sup>6</sup>Northwestern University, USA — <sup>7</sup>FLASH@DESY — <sup>8</sup>Kansas State University, USA — <sup>9</sup>optiX fab, Jena

Coherent diffraction experiments using intense femtosecond short-wavelength pulses from free-electron lasers (FEL) allow to determine the structure and dynamics of individual nanoparticles. The ultrafast ionization and fragmentation dynamics of large methane clusters were studied using intense XUV double pulses from the split-and-delay unit DESC at the FLASH FEL (DESY Hamburg). With each double pulse both the cluster's initial state, and 35-650 picoseconds later the ionized state, are imaged separately on a two-detector setup. Ionic fragments are measured in coincidence with a time-of-flight spectrometer. Methane clusters, as heterogeneous model systems for biomolecules, reveal rich dynamics of higher adducts [Iwan *et al.* (2012) PRA **86**, 033201], unobserved in molecular methane or homogeneous clusters. The dependence of the ion spectra on cluster size and time delay will be discussed.

MO 17.19 Wed 16:15 Orangerie

**THz/IR spectroscopy of glycine-water in helium nanodroplets** — ●NITISH PAL<sup>1</sup>, DEVENDRA MANI<sup>1</sup>, RAFFAEL SCHWAN<sup>1</sup>, GERHARD SCHWAAB<sup>1</sup>, BRITTA REDLICH<sup>2</sup>, LEX VAN DER MEER<sup>2</sup>, and MARTINA HAVENITH<sup>1</sup> — <sup>1</sup>Physikalische Chemie II, Ruhr-Universität Bochum, Germany — <sup>2</sup>Institute for Molecules and Materials (IMM), Radboud University Nijmegen, Nijmegen, Netherlands

It is well known that glycine exists in the neutral form in gaseous state and in the zwitterionic form in aqueous solution. Numerous experimental [1] and theoretical [2] studies have been carried out to understand this transformation. One of the most important goals has been to determine the minimum number of water molecules needed for such transformation.

We have already reported infrared spectra of glycine and 1:1 glycine-water complexes [3], now we are exploring the intermolecular proton transfer mechanism by stepwise adding water molecules to glycine molecule in helium droplets. The superfluid medium of helium nanodroplets allows a barrier-free diffusion of the dopant molecules and enables the formation of molecular clusters at 0.37 K temperature. The experiments are carried out using helium nanodroplet spectroscopy technique in combination with Free Electron Laser (FEL) at FELIX laboratory in Nijmegen. Herein we present the results of glycine-water infrared absorption spectra.

- [1] Espinoza, C *et al.*, J. Phys. Chem. A., **114**, 5919, (2010).  
 [2] Tudela, R *et al.*, J. Phys. Chem. Lett., **7**, 5137, (2016).  
 [3] Kaufmann, M *et al.*, Phys. Chem. Chem. Phys., **18**, 28082, (2016).

## MO 18: Clusters IV (joint session MO/A)

Time: Thursday 10:30–12:15

Location: PA 2.150

### Invited Talk

MO 18.1 Thu 10:30 PA 2.150

**Untersuchungen zur Coulomb-Wechselwirkung bei polyanionischen Metallclustern** — MADLEN MÜLLER<sup>1</sup>, ●FRANKLIN MARTINEZ<sup>2</sup>, NORMAN IWE<sup>2</sup>, KLARA RASPE<sup>2</sup>, STEFFI BANDELOW<sup>1</sup>, JOSEF TIGGESBÄUMKER<sup>2</sup>, LUTZ SCHWEIKHARD<sup>1</sup> and KARL-HEINZ MEIWES-BROER<sup>2</sup> — <sup>1</sup>Institut für Physik, E.-M.-A.-Universität Greifswald, Felix-Hausdorff-Str. 6, 17489 Greifswald — <sup>2</sup>Institut für Physik, Universität Rostock, Albert-Einstein-Str. 23-24, 18059 Rostock

Der Ladungszustand ist ein wichtiger Parameter beim Studium der elektronischen Eigenschaften freier, nanoskopischer Teilchen. Im Falle mehrfach negativ geladener Metallcluster beeinflusst vor allem die Coulomb-Wechselwirkung zwischen den Valenzelektronen die Clustereigenschaften. So spielt bei den hier betrachteten Polyanionen der Coulombwall eine wichtige Rolle, sowohl bei der Aufladung, d.h. der

Elektronenanlagerung, als auch bei der Elektronenemission. Die Eigenschaften dieses Coulombwalls sind jedoch noch weitgehend ungeklärt und stehen vermutlich in komplexen Abhängigkeiten von beispielsweise der Clusterform oder von elektronischen Korrelationen. In diesem Beitrag werden Untersuchungen zur Coulomb-Wechselwirkung anhand erstmalig gemessener Photoelektronenspektren von polyanionischen Metallclustern vorgestellt. Dabei bietet insbesondere der Verlauf der gemessenen Energieverteilungen einen Zugang zur Clustergrößen- und Ladungszustandsabhängigkeit des Coulombwalls. Die experimentellen Beobachtungen werden mit Abschätzungen aus dem Metallkugel- und dem Jellium-Modell verglichen.

MO 18.2 Thu 11:00 PA 2.150

**Elektronenaffinitäten von polyanionischen Metallclustern** — ●MADLEN MÜLLER<sup>1</sup>, FRANKLIN MARTINEZ<sup>2</sup>, STEFFI BANDELOW<sup>1</sup>,

NORMAN IWE<sup>2</sup>, KLARA RASPE<sup>2</sup>, JOSEF TIGGESBÄUMKER<sup>2</sup>, LUTZ SCHWEIKHARD<sup>1</sup> und KARL-HEINZ MEIWES-BROER<sup>2</sup> — <sup>1</sup>Institut für Physik, E.-M.-A.-Universität Greifswald, Felix-Hausdorff-Str. 6, 17489 Greifswald, Deutschland — <sup>2</sup>Institut für Physik, Universität Rostock, Albert-Einstein-Str. 23-24, 18059 Rostock, Deutschland

Die Photoelektronenspektroskopie von Metallclustern, bislang vorrangig an einfach negativ geladenen Systemen durchgeführt, gibt Aufschluss über Elektronenaffinitäten (EA) und die elektronische Struktur. Im Bezug auf polyanionische Systeme sollte sich die EA mit zunehmendem Ladungszustand erheblich ändern, da in einem einfachen Bild die Coulombenergie das Jelliumpotenzial anhebt, unter Umständen, bis über das Vakuumniveau hinaus.

Erstmals werden massenselektierte Metallcluster mit bis zu 800 Atomen und sieben zusätzlichen Elektronen in einer linearen Paulifalle produziert. Von diesen polyanionischen Systemen werden Photoelektronenspektren aufgenommen und Schwellenwerte d.h. Elektronenaffinitäten der negativen Ladungszustände bestimmt. Insbesondere werden dabei metastabil gebundene Elektronen über ihre negative Bindungsenergie nachgewiesen. Das Verhalten der Schwellenwerte in Abhängigkeit von Clustergröße und Ladungszustand wird vorgestellt und diskutiert. Das Projekt wurde durch den Sonderforschungsbereich 652 der DFG unterstützt.

MO 18.3 Thu 11:15 PA 2.150

**Magnetic-quantum-state-selected metastable helium atoms for Penning reaction studies** — ●SIMON HOFSSÄSS, JONAS GRZEŚIAK, FRANK STIENKEMEIER, and KATRIN DULITZ — University of Freiburg

Our experiments are aimed at studying the influence of electron-spin polarization on the Penning reaction rate between supersonically expanded metastable helium atoms and ultracold lithium atoms confined in a magneto-optical trap (MOT). In our experiments, we plan to selectively focus the He( $2^3S_1$ ,  $M_J = 1$ ) state into the stationary MOT target using magnetic hexapoles in a Halbach configuration. We present first experimental results which clearly show that a beam of metastable helium atoms can be steered using magnetic hexapole focusing, and we compare these results to the outcome of particle trajectory simulations.

MO 18.4 Thu 11:30 PA 2.150

**Optical properties of small cationic aluminium clusters and (Al<sub>7</sub>)-(1-adamantanethiol)<sup>+</sup> hybrid systems** — ●ANDRE KNECHT<sup>1</sup>, POLINA LISINETSAYA<sup>2</sup>, TOBIAS BISCHOFF<sup>1</sup>, ANDREA MERLI<sup>1</sup>, THOMAS MÖLLER<sup>1</sup>, TOBIAS LAU<sup>3</sup>, BERND VON ISSENDORFF<sup>4</sup>, ROLAND MITRIC<sup>2</sup>, and TORBJÖRN RANER<sup>1</sup> — <sup>1</sup>IOAP, Technische Universität Berlin — <sup>2</sup>Institut für physikalische und theoretische Chemie, Universität Würzburg — <sup>3</sup>Helmholtz Zentrum Berlin — <sup>4</sup>Physikalisches Institut, Universität Freiburg

Radiative processes, such as fluorescence or Raman-scattering can be modified by the presence of a nearby metal[1]. While on the macroscopic such processes are well understood, our knowledge on the molecular level is sparse. Here we present results on hybrids consisting of a small metal cluster, Al<sub>7</sub><sup>+</sup>, and an anorganic cluster, a thiolized diamondoid. Diamondoids, sp<sup>3</sup>-hybridized, hydrogen passivated subnanometer-sized carbon-cages serve as a UV absorbent and fluorescent species in the hybrid system. Mass selectable aluminium clus-

ter cations act as the UV plasmonic host with size-dependent band energies. To attach adamantane, the smallest diamondoid, to the metal cluster a molecular linker (SH) was used. This combination was chosen, because the plasmon resonance of the Al cluster energetically overlaps with the stray absorption bands of 1-adamantanethiol. The monodisperse clusters were generated and investigated in the gas phase using partial ion yield spectroscopy. We show first results, as well as a TD-DFT analysis of the data.

[1]Tam et al., Nano letters 7.2 (2007):496-501

MO 18.5 Thu 11:45 PA 2.150

**Velocity Map Imaging of the Photo-induced Dissociation of Mass-selected Cation Complexes** — ●DANIEL LEICHT, BRANDON M. RITTGERS, and MICHAEL A. DUNCAN — University of Georgia, Athens, USA

We employ a velocity map imaging mass spectrometer to study the photo-induced dissociation of mass-selected ionic molecular complexes. Ions are produced in a molecular beam and pulse extracted in a linear time-of-flight mass spectrometer. After mass selection, the ions are intersected with a laser beam, leading to dissociation. The fragments are then detected with spatial resolution by multichannel plates and a phosphor screen. From the spatial distribution of fragments we can extract the kinetic energy release of the dissociation process.

Excitation of Ag<sup>+</sup>-benzene and Ag<sup>+</sup>-toluene with 355 nm leads to the exclusive formation of benzene<sup>+</sup> and toluene<sup>+</sup> fragments, respectively. This is indicative of a dissociative charge transfer process. On the other hand, irradiation of Zn<sup>+</sup>-acetylene with 266 nm leads to the formation of both, Zn<sup>+</sup> and acetylene<sup>+</sup> fragments. Apparently, two different photo-initiated dissociation pathways take place in this system.

The observed kinetic energy release in all of these systems can provide information about the binding energy and, given sufficient resolution, the population of quantum states in the fragment ions.

MO 18.6 Thu 12:00 PA 2.150

**Nanodroplet production and characterization** — ●AMINE GOURRAM<sup>1</sup>, ARMANDO ESTILLORE<sup>1</sup>, DANIEL HORKE<sup>1,3</sup>, and JOCHEN KUEPPER<sup>1,2,3</sup> — <sup>1</sup>Center for Free-Electron Laser Science, DESY, Hamburg, Germany — <sup>2</sup>Department of Physics, Universität Hamburg, Hamburg, Germany — <sup>3</sup>The Hamburg Center for Ultrafast Imaging, Universität Hamburg, Hamburg, Germany

X-ray diffractive imaging of single molecules or nanoparticles at free-electron lasers allows the extraction of structural information at sub-nanometer resolution [1]. However, this requires the efficient production and delivery of isolated samples into the x-ray beam. We present our proposed aerosol source for the efficient production of a high-density aerosol of sub-100 nm nanoparticles, based on electrospray aerosolisation. The produced aerosol source will be characterized regarding its efficiency and density for different nanoparticle types and sizes using optical light scattering measurement [2] and differential particle mobility analysers.

[1] Seibert et al., Nature **470**, 78-81 (2011)

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

## MO 19: Annual General Meeting of the Molecular Physics Division

Time: Thursday 12:30–13:15

Location: PA 2.150

Duration 45 min.

## MO 20: Resonant Energy Transfer and Interatomic Coulombic Decay I

Time: Thursday 14:00–15:45

Location: PA 1.150

**Invited Talk** MO 20.1 Thu 14:00 PA 1.150  
**Energy and charge transfer processes in helium nanodroplets** — ●MARCEL MUDRICH — Department of Physics and Astronomy, Aarhus University, Denmark

Currently the focus is shifting towards ICD and related interatomic decay processes occurring in more complex media such as biomolecules and condensed phase systems. In this respect, pure and doped helium

nanodroplets offer interesting perspectives: They have a homogenous, superfluid density, and they are able to embed, aggregate, and cool atoms and molecules, while their constituents are simple two-electron atoms. Thus helium droplets are ideal for tailoring all kinds of unsupported hetero-complexes.

I will report on our recent experiments probing ICD, ETMD, and related correlated decay processes in pure and doped helium nanodroplets initiated by cw or pulsed EUV radiation. In particular, we

find that multiple ionization of embedded species can be either facilitated or hampered by the surrounding helium nanodroplets.

MO 20.2 Thu 14:30 PA 1.150

**Superexchange Interatomic Coulombic Decay: a bridged assisted mechanism** — ●NICOLAS SISOURAT<sup>1</sup>, TSVETA MITEVA<sup>1</sup>, SÉVAN KAZANDJIAN<sup>1</sup>, PETRA VOTAVOVÁ<sup>2</sup>, and PŘEMYSL KOLOREŇČ<sup>2</sup> — <sup>1</sup>Sorbonne Universités, UPMC Univ Paris 06, UMR 7614, Laboratoire de Chimie Physique Matière et Rayonnement, F-75005 Paris, France — <sup>2</sup>Charles University, Faculty of Mathematics and Physics, Institute of Theoretical Physics, V Holešovičkách 2, 180 00 Prague, Czech Republic

Interatomic Coulombic Decay (ICD) is an ultrafast energy transfer process. Via ICD, an excited atom can transfer its excess energy to a neighboring atom which is thus ionized.

The rates of ICD depend on the distance between the interacting species. At large interatomic distances  $R$ , the process can be viewed as an exchange of a virtual photon between the interacting species. In this so-called virtual photon exchange mechanism the decay rates display a  $1/R^6$  dependence.

We recently demonstrated that the ICD rates are substantially enhanced in the presence of an ICD inactive atom, i.e. an atom whose ionization potential is greater than the excess energy of the excited species. This enhancement occurs due to coupling of the resonance state to intermediate virtual states of the bridge atom.

During the talk, I will present the Fano-Stieltjes method we employed for computing the ICD rates. Accuracy of the method will be shortly discussed. Finally, some examples illustrating this novel mechanism will be reported.

MO 20.3 Thu 14:45 PA 1.150

**Light induced inter-Coulombic decay in quantum dots controlled via laser focus, field strength, and polarization** — ●ANIKA HALLER and ANNIKA BANDE — Institute of Methods for Material Development, Helmholtz-Zentrum Berlin für Materialien und Energie, Albert-Einstein-Str. 15, 12489 Berlin, Germany

The inter-Coulombic decay (ICD), an ultrafast energy transfer process induced by long-range electron correlation, has been shown to take place in pairs of atom-like nanostructures, namely quantum dots (QD). We theoretically investigate the electron dynamics for a system of two singly-charged non-coupled GaAs QDs. After resonant excitation by a laser pulse the system efficiently decays from its resonance excited state via ICD: inter-QD energy transfer causes excitation of one electron from one QD into the continuum, while the other relaxes to a lower bound state of the other QD. We show the field strength dependence of the ICD initiation including a changing number of Rabi oscillations during population. In addition, we study the impact of the laser focus on the second, direct ionization channel. Furthermore, we analyze the effect of electric field polarization on the efficiency of ICD, and thus open up the applicability in a further group of material systems. A space-resolved wavefunction ansatz is applied by means of the antisymmetrized multiconfiguration time-dependent Hartree method (MCTDH). A state-resolved representation has been developed as an alternative approach, which lets us conclude on the importance of multi-photon processes.

MO 20.4 Thu 15:00 PA 1.150

**Calculating Interatomic Coulombic Decay Rates from Atomic Data: A case study** — ●SEVERIN BANG<sup>1</sup>, ROBERT BENNETT<sup>1</sup>, and STEFAN YOSHI BUHMANN<sup>1,2</sup> — <sup>1</sup>University of Freiburg, Germany — <sup>2</sup>Freiburg Institute for Advanced Studies (FRIAS), Freiburg, Germany

Interatomic Coulombic decay is an ultra-fast decay process by which energy can be transported between molecules. There are two main approaches to the calculation of the ICD rate, namely ab initio quantum

chemistry simulations, or in terms of atomic transitions with their associated photon emission and absorption. In this talk, I will discuss the intricacies of the process by which ICD rates can be calculated from atomic line data. The whole ICD process begins with a donor species being in an excited state, followed by a relaxation and the corresponding photon emission, which in turn ionises an acceptor species.

The ultimate aim of this work is to critically evaluate the ability of currently available spectral line data to give reliable predictions for ICD. Using data from the NIST spectral line database, we will show an example calculation for a neon-argon cluster. We will also point out cases where the data necessary for such investigations is incomplete. For some transitions, no dipole moments are available, and the photoionization cross-section data is very sparse. Finally, we compare our asymptotic ICD rates with those from ab initio approaches, noting that the latter experience difficulties when taking the large-separation limit of initially composite systems.

MO 20.5 Thu 15:15 PA 1.150

**Ultrafast proton migration in water and ice** — ●CLEMENS RICHTER<sup>1</sup>, CLARA SAAK<sup>2</sup>, MELANIE MUCKE<sup>2</sup>, ISAAK UNGER<sup>2</sup>, MINNA PATANEN<sup>3</sup>, TORSTEN LEITNER<sup>4</sup>, IEVA BIDERMANE<sup>4</sup>, CASPAR LANT<sup>1,4,5</sup>, OLLE BJÖRNEHOLM<sup>2</sup>, and UWE HERGENHAHN<sup>1,6</sup> — <sup>1</sup>Leibniz-Institut für Oberflächenmodifizierung, Leipzig — <sup>2</sup>Uppsala University, Sweden — <sup>3</sup>University of Oulu, Finland — <sup>4</sup>Helmholtz-Zentrum Berlin — <sup>5</sup>New York University, NY USA — <sup>6</sup>Max-Planck-Institut für Plasmaphysik, Greifswald

Inner-shell ionization of water leads not only to a  $K$ -shell decay, but also to a substantial nuclear rearrangement. A spectral signature for ultrafast proton transfer has been seen in Auger and X-Ray spectra of liquid water. Detailed theoretical modelling has revealed the role of Intermolecular Coulombic Decay (ICD) and Electron Transfer Mediated Decay (ETMD) in these spectra. An analogous feature we now have observed in  $KVV$  Auger spectra of amorphous ice. To minimize charging and radiation damage, we have employed an angle-resolving time-of-flight spectrometer offering a large collection angle for electrons together with good energy resolution at Auger kinetic energies.

In a second set of experiments, we intended to use the proton transfer signature ('proton transfer mediated charge separation', PTMCS) as a monitor for hydrogen bond strength in a variety of systems. Towards this end, we have recorded the  $K$ -shell autoionization spectra of water clusters in comparison with methanol clusters, which are known to have a less strong hydrogen network. Several cluster sizes were probed. Differences between the two species will be discussed.

MO 20.6 Thu 15:30 PA 1.150

**Recent Progress in the Theoretical Description of the Inter-Particle Coulombic Decay in Paired Metal Nanoparticle - Quantum Dot Systems** — ●MATTHIAS BERG<sup>1</sup>, ALIEZER MARTÍNEZ-MESA<sup>2</sup>, LLINERSY URANGA-PIÑA<sup>2</sup>, and ANNIKA BANDE<sup>1</sup> — <sup>1</sup>Helmholtz-Zentrum Berlin für Materialien und Energie, Hahn-Meitner Platz 1, 14109 Berlin, Germany — <sup>2</sup>DynAMoS (Dynamical processes in Atomic and Molecular Systems), Faculty of Physics, University of Havana, Cuba

Metal nanoparticles (MNPs) and semiconductor quantum dots (QDs) are two of the main building blocks of nano-scale systems with a wide range of applications in electronics and photonics. In view of the ubiquitous nature of the interparticle Coulombic decay process (ICD), which was also studied for paired QDs, we investigate ICD in the context of MNP-QD dimers. In this proposed scenario, the MNP is excited to a plasmonic state, which drives the emission of an QD electron. The energy transfer between the systems is mediated by the long-range Coulomb interaction. I will report on new developments towards a time-dependent description of the process, based upon the established electron dynamics methodology for paired QDs.

## MO 21: Advanced Time-Resolved Spectroscopy

Time: Thursday 14:00–15:45

Location: PA 2.150

MO 21.1 Thu 14:00 PA 2.150

**Broadband fluorescence-detected one- and two-quantum 2D electronic spectroscopy** — ●STEFAN MÜLLER, SIMON DRAEGER, XIAONAN MA, MATTHIAS HENSEN, and TOBIAS BRIXNER — Institut für Physikalische und Theoretische Chemie, Universität Würzburg,

Am Hubland, 97074 Würzburg, Germany

We developed a single-beam setup for 2D electronic spectroscopy in the liquid phase using fluorescence as an observable [1]. Collinear femtosecond phase-modulated pulse trains are generated by an acousto-optic dispersive filter on a 1 kHz shot-to-shot basis. Broadband excitation

in the visible spectral range is provided by the supercontinuum output of an argon-filled hollow-core fiber. By utilizing phase cycling we demonstrate the simultaneous acquisition of different nonlinear signal contributions such as photon-echo, two-quantum coherence and one-quantum-two-quantum signals without nonresonant solvent response or scattering artifacts that pose a substantial challenge in noncollinear coherence-detected 2D spectroscopy. We show that information about nuclear wave-packet dynamics, doubly excited states as well as coupling between excited states can be received from these nonlinear signals.

[1] S. Draeger, S. Roeding, and T. Brixner, *Opt. Express* **25**, 3259 (2017).

MO 21.2 Thu 14:15 PA 2.150

**Diffusion Controlled Singlet Fission of a Tetracene Derivative in Solution** — ●NIKOLAUS WOLLSCHIED<sup>1</sup>, NICOLÒ ALAGNA<sup>1</sup>, JOSÉ LUIS PEREZ LUSTRES<sup>1</sup>, TIAGO BUCKUP<sup>1</sup>, SEBASTIAN HAHN<sup>2</sup>, UWE BUNZ<sup>2</sup>, and MARCUS MOTZKUS<sup>1</sup> — <sup>1</sup>Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg — <sup>2</sup>Organisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg

Singlet fission (SF) is the process by which one excited singlet state yields two triplet states upon close interaction of two chromophores. This ultrafast photoreaction was first observed in solid state and has strong implications in organic photovoltaics [1]. SF was also reported in concentrated solutions, where the diffusion of the reaction partners extends the dynamics to longer timescales [2]. This eases the identification of the involved species and helps to disentangle the mechanism. In this work, we use ultrafast transient absorption (TA) spectroscopy to investigate concentrated solutions of an aza-substituted tetracene derivative in toluene. Measurements at different concentrations show: a) the correlation between singlet decay and triplet formation and b) acceleration of the reaction dynamics with increasing concentration. Both observations together indicate a diffusion mediated SF process. Spectral analysis suggests a kinetic model involving an intermediate TT state.

[1] M. Smith and J. Michl, *Chem. Rev.*, **110**, 6891, (2010)

[2] B. Walker, A. J. Musser, D. Beljonne, R. Friend, *Nat. Chem.*, **5**, 1019 (2013)

MO 21.3 Thu 14:30 PA 2.150

**Exciton diffusion in molecular aggregates characterized by exciton-exciton interaction spectroscopy** — ●JAKUB DOSTÁL<sup>1</sup>, FRANZISKA FENNEL<sup>2</sup>, FEDERICO KOCH<sup>1</sup>, STEFANIE HERBST<sup>2</sup>, FRANK WÜRTHNER<sup>2</sup>, and TOBIAS BRIXNER<sup>1</sup> — <sup>1</sup>Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg — <sup>2</sup>Institut für Organische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

An essential part of natural and artificial light harvesting is the efficient transport of excitation energy. In molecular aggregates it often proceeds as random diffusion of excitons delocalized over several aggregate sites. Random encounters of two excitons lead to a rapid annihilation of one of them due to internal conversion. Tracking the number of such events as a function of population time and excitation intensity can provide valuable information on the timescale of exciton diffusion.

In our contribution we study exciton diffusion in one-dimensional J-aggregates of a perylene bisimide (PBI) dye by means of exciton-exciton interaction 2D spectroscopy (EEI2D). This recently developed spectroscopic technique is able to single out the signal specific to interactions between exciton pairs. We observed that the EEI2D signal of the studied PBI aggregates consists of the diffusion-enabled exciton annihilation and the direct excitation of the two exciton states. Theoretical modeling of time evolution of the EEI2D signal allowed us to determine the exciton diffusion constant and estimate the exciton delocalization length.

MO 21.4 Thu 14:45 PA 2.150

**Optical Properties of Single Mikrometer Dye Crystals** — ●CHRIS REHHAGEN, STEFFEN WOLTER, and STEFAN LOCHBRUNNER — University of Rostock, Germany

Dye crystals are of rising interest in opto-electronic applications, especially due to potentially large exciton mobilities. Furthermore, crystals provide stable and regular structures which are well suited for common characterization methods. In this work, small crystals in the range of 10 – 500  $\mu\text{m}$  are prepared from solutions of the dyes TTBC, Coumarin153 and Perylen Orange. To investigate their optical properties a microscope with a resolution of 30  $\mu\text{m}$  is implemented for single-

crystal absorption and fluorescence spectroscopy. The setup is also combined with a streak camera in order to investigate the dynamics of electronic excitations. Beyond this, FLIM is used to investigate the lifetime distribution down to a spatial resolution of 200  $\text{nm}$ . The results show that there is a connection between the macroscopic structure of the crystals and their optical properties. Especially some TTBC crystals show fluorescence spectra with spectrally narrow components typical for J-type aggregation and a lifetime in the range of tens of picoseconds.

MO 21.5 Thu 15:00 PA 2.150

**Structure and dynamics of water at the electrolyte solution-air interface studied with pump-probe SFG** — ●MALTE DEISEROTH, SUDIPTA DAS, MISCHA BONN, and ELLEN H.G. BACKUS — Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz

Physical and chemical processes occurring at salt-water-air interfaces play a prominent role in a variety of fields ranging from the chemistry of atmospheric aerosols and heterogeneous catalysis to biophysics and biochemistry. Knowledge of the molecular interfacial structure and energy flow dynamics at these interfaces is important, not only for a fundamental understanding of this ubiquitous liquid but also to understand its reactivity.

Here, we report a surface-sensitive sum-frequency generation (SFG) spectroscopy study of the interface of electrolyte solutions with air, aimed at obtaining information about the molecular arrangement of water and ions at the interface, and how this affects energy dissipation at the interface. Time-resolved and 2D pump-probe spectroscopy provide insights into dynamics of interfacial water molecules with sub-picosecond time resolution. Substantial differences are observed between the static SFG spectra obtained from the surface of solutions of  $\text{Na}_2\text{SO}_4$ ,  $\text{Na}_2\text{CO}_3$ , and pure water, pointing to large variations in the interfacial structure of these different solutions; remarkably, the vibrational dynamics of these systems are indistinguishable. Hence, while electrolytes clearly restructure the interface of water, the vibrational dynamics is unaffected by the structural changes.

MO 21.6 Thu 15:15 PA 2.150

**Ultrafast Vibrational Relaxation of Water at the Ice - Air Interface** — ●PRERNA SUDERA, JENÉE D CYRAN, ALEJANDRA MARIA SÁNCHEZ, MISCHA BONN, and ELLEN H. G. BACKUS — Max Planck Institute for Polymer Research, Mainz, Germany

For chemical reactions occurring on the ice surface - relevant for e.g. atmospheric reactions - the dynamics of the surface water molecules and energy flow pathways play an important role: following a chemical reaction, the rate of dissipation of excess energy determines the probability of a back-reaction occurring. Here we elucidate the relaxation dynamics of water molecules at the surface of single crystalline hexagonal ice after exciting the O-H stretch vibration and compare our results with the relaxation dynamics of the liquid water-air interface.

To study the vibrational dynamics we apply time-resolved sum frequency generation spectroscopy. With this method, we can vibrationally excite the surface molecules with a femtosecond infrared excitation pulse, and probe the dynamics of the interfacial molecules with the SFG process using a visible and an infrared pulse resonant with the O-H stretch vibrations. This detection scheme ensures that only the interfacial water molecules contribute to the signal; the use of  $\sim 50$  fs laser pulses ensures high time resolution in the experiments.

Our results show that the relaxation dynamics of the O-H stretch mode after excitation at 3100  $\text{cm}^{-1}$  at the basal plane of ice is around 70 fs - three times faster than for the water-air interface. We discuss the origins and implications of ultrafast energy dissipation at ice interfaces, compared to the liquid.

MO 21.7 Thu 15:30 PA 2.150

**Shaper based infrared spectroscopy in a nonlinear Raman setup** — ●NIKLAS MÜLLER, LUKAS BRÜCKNER, and MARCUS MOTZKUS — Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, 69120 Heidelberg

The infrared and Raman sensitivities differ for a vibrational transition, particularly in molecules with inversion symmetry. Therefore a combination of both methods yields to more information about the molecules. Combining the established coherent anti-Stokes Raman scattering (CARS) setup [1] with a tunable narrowband infrared light source, we are able to do both CARS and infrared spectroscopy in a single-beam setup. Broadband laser pulses spectrally centered at 800 nm are shaped by a liquid crystal spatial light modulator to gen-

erate either background-free coherent anti-Stokes signal in a sample or narrowband tunable infrared light in a birefringent crystal beforehand. The infrared light is generated by difference-frequency generation in a thin LiIO<sub>3</sub> crystal by phase and polarization shaped laser pulses. On the one hand, the large tunability ( $>1500\text{ cm}^{-1}$ ) is based on the broad

phase matching condition of the thin crystal. On the other hand, the narrowband behavior ( $<25\text{ cm}^{-1}$ ) is achieved by chirped laser pulses yielding to the same instantaneous frequency difference in the crystal. [1] L. Brückner, et al. *JOSA B* 33 1482 (2016)

## MO 22: Posters 3: Experimental and Theoretical Techniques and High Resolution Spectroscopy

Time: Thursday 16:15–18:15

Location: Zelt West

MO 22.1 Thu 16:15 Zelt West

**Fast-timing-readout for a micro-calorimeter particle detector** — ●SEBASTIAN SPANIOL<sup>1</sup>, OLDŘICH NOVOTNÝ<sup>1</sup>, STEFFEN ALLGEIER<sup>2</sup>, CHRISTIAN ENSS<sup>2</sup>, ANDREAS FLEISCHMANN<sup>2</sup>, LISA GAMER<sup>2</sup>, DENNIS SCHULZ<sup>2</sup>, and ANDREAS WOLF<sup>1</sup> — <sup>1</sup>Max Planck Institute for Nuclear Physics, Heidelberg, Germany — <sup>2</sup>Kirchhoff Institute for Physics, Heidelberg, Germany

For the Cryogenic Storage Ring (CSR) we are developing the molecule camera MOCCA, a micro-calorimeter based particle detector for mass-resolved detection of electrically neutral molecular fragments, originating from molecular-ion collisions on electrons, photons, etc. 3D imaging will be employed to determine the kinetic energy released in the fragmentation. Here the transverse position sensitivity is provided by the segmentation of the detector into 64 x 64 pixels onto a detection area of 45mm x 45mm. For impact time measurement on a ns scale we are developing a fast-timing-readout of secondary electrons. We discuss simulations of the employed electrostatic transport system, qualitatively approving the proposed concept and leading to a detailed mechanical design.

MO 22.2 Thu 16:15 Zelt West

**Cost effective time-to-digital and high repetition rate boxcar averager for efficient signal processing** — ●DANIEL UHL, LUKAS BRUDER, VLADYSLAV TYZHNEVYI, KAMBIZ MAHBOUBI, and FRANK STIENKEMEIER — Physikalisches Institut, Universität Freiburg, Hermann-Herder Str. 3, 79104 Freiburg

The development in ultrafast spectroscopy generally tends towards higher laser repetition rates ( $>100\text{kHz}$ ), which requires fast signal processing. Many measurement schemes require boxcar averagers to isolate the spectroscopic signatures of interest. Commercially available devices for high repetition rates are, however, expensive. Likewise, digitizing signal traces, e.g. time-of-flight (TOF) traces, require typically fast ( $\geq 1\text{GSa/s}$ ), fairly expensive digitizers. In addition, fully digitized traces often contain redundant information (many zeros) but produce large datasets that are impractical for real-time signal processing. Here, time-to-digital converters (TDC) provide an optimal solution. We are developing a combined cost-effective solution for TDC and boxcar applications implemented in a field programmable gate array (FPGA). Our device provides TDC with high timing precision and multiple hit modus, as well as a boxcar averager with a high repetition rate and multiple gates.

MO 22.3 Thu 16:15 Zelt West

**An electron UV/VIS-photon coincidence set-up using a magnetic bottle and a position sensitive photon detector** — ●CHRISTIAN OZGA<sup>1</sup>, GREGOR HARTMANN<sup>1</sup>, PHILIPP SCHMIDT<sup>1</sup>, CLEMENS RICHTER<sup>2,3</sup>, ANDREAS HANS<sup>1</sup>, UWE HERGENHAHN<sup>3,4</sup>, ARNO EHRESMANN<sup>1</sup>, and ANDRÉ KNIE<sup>1</sup> — <sup>1</sup>Institut für Physik und CINSaT, Universität Kassel, Heinrich-Plett-Straße 40, 34132 Kassel, Germany — <sup>2</sup>Department of Physics, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany — <sup>3</sup>Leibniz Institute of Surface Modification (HZB-IOM Joint-Photonic Lab), Permoserstr. 15, 04318 Leipzig, Germany — <sup>4</sup>Max Planck Institute for Plasma Physics, Wendelsteinstr. 1, 17491 Greifswald, Germany

Here we present a set-up for the detection of photons in the wavelength regime from 200 nm to 680 nm which are measured in coincidence with electrons having kinetic energies as low as 0.5 eV up to a few hundred eV using a magnetic bottle electron spectrometer. While the collection efficiency of the emitted electrons is drastically increased by this type of electron spectrometer it is also possible to use a set of mirrors and lenses to increase the solid angle for the photon collection resulting in a much higher efficiency of the coincidence measurement. Furthermore, the usage of lenses allows to guide the emitted photons

which increases the flexibility and versatility of the photon detection. While this set-up can be used for the investigation of liquid samples, we demonstrate the feasibility of the experiment using the well-known Neon 1s photoexcitation as a proof-of-principle.

MO 22.4 Thu 16:15 Zelt West

**A magnetic bottle spectrometer for 2D electronic spectroscopy experiments in the gas phase** — ●MAX JAKOB, LUKAS BRUDER, MARCEL BINZ, DANIEL UHL, ULRICH BANGERT, and FRANK STIENKEMEIER — Physikalisches Institut, Universität Freiburg, Hermann-Herder Str. 3, 79104 Freiburg

2D electronic spectroscopy (2DES) is a powerful tool to study complex dynamics in real time. While most 2D studies have been conducted in the condensed phase, we have built an apparatus to perform 2DES experiments on molecular and cluster beams in the gas phase. As an advantage, our setup can be combined with energy-resolved photoelectron detection, which basically adds an additional dimension to the 2D spectra. For this purpose, we have constructed a magnetic bottle spectrometer, which provides high collection efficiencies for photoelectrons. Binding energies are deduced from time-of-flight efficiently processed with time-to-digital conversion and combined with lock-in detection to increase the sensitivity.

MO 22.5 Thu 16:15 Zelt West

**New beamlines for molecular pump-probe experiments in the XUV and SXR** — MATTHEW ROBINSON, ●CHRISTIAN MATTHAEI, and MARKUS GÜHR — Institut für Physik und Astronomie, Universität Potsdam

Until recently the only place to perform pump-probe experiments with femtosecond Soft X-Ray (SXR) probe pulses was at the few large X-ray Free Electron Laser (XFEL) facilities, like the Linac Coherent Light Source (LCLS) and the European XFEL. With recent innovations in the field of High Harmonic Generation (HHG) it has become possible to create photons with energies in excess of the carbon K-edge [1,2,3], thus allowing time resolved X-ray probing in a small lab setting.

We are currently constructing such a set-up at Potsdam University, which will be used for the study of small molecules in the gas phase. Extreme UV and SXR pulses are produced using HHG, followed by a set-up for time-resolved atom-specific spectroscopy. In these studies a thorough understanding of nonadiabatic molecular dynamics is our goal.

[1] S. L. Cousin et al., *Optics Letters*, 39, pp. 5383-5386, 2014

[2] Y. Pertot et al., *Science*, 355, pp. 264-267, 2017

[3] T. Popmintchev et al., *Science*, 336, pp. 1287-1291, 2012

MO 22.6 Thu 16:15 Zelt West

**An ultrafast electron diffraction setup for molecules in aqueous solution** — ●ARNE UNGEHEUER, ARNE SENFTLEBEN, MARLENE ADRIAN, and THOMAS BAUMERT — Institut für Physik, Universität Kassel, Heinrich-Plett-Straße 40, 34132 Kassel, Deutschland

Here we present a scheme for an ultrafast electron diffraction setup for electron diffraction on liquids and particles in aqueous solution. We adapt the idea to use two obliquely colliding single laminar jets for the creation of a leaf-shaped flatjet with sub-micrometer thickness required for electron diffraction in transmission mode. The issue of multiple scattering in these relatively thick samples is addressed by the use of an energy-filter to increase the signal-to-noise ratio. Preliminary measurements of the liquid jet thickness and stability regimes under ambient conditions are shown.

MO 22.7 Thu 16:15 Zelt West

**Experimental set-up for electron impact induced luminescencespectroscopy of a liquid microjet** — ●DANA BLOSS<sup>1</sup>, AN-

DREAS HANS<sup>1</sup>, CHRISTIAN OZGA<sup>1</sup>, PHILIPP SCHMIDT<sup>1</sup>, MASATOSHI UKAI<sup>2</sup>, ARNO EHRESMANN<sup>1</sup>, and ANDRÉ KNEI<sup>1</sup> — <sup>1</sup>Institut für Physik und CINSaT, Universität Kassel, Heinrich-Plett-Straße 40, 34132 Kassel — <sup>2</sup>Department of Applied Physics, Tokyo University of Agriculture and Technology, Koganei-shi, Tokyo 184-8588, Japan

The liquid microjet technique allows the investigation of a variety of different targets ranging from pure liquids to solutions which mimic biological systems. While most experiments use photon excitation, other methods such as electron impact can offer an additional insight due to a broadband excitation. Here we present an experimental set-up for the measurement of dispersed luminescence of liquid microjets induced by electron impact with keV kinetic energy. These measurements provide a comparison with the photon-induced luminescence spectra. Perspectively this set-up can be used to investigate the behaviour and interaction of solvated (bio-) molecules as function of the penetration depth of the primary electron beam.

MO 22.8 Thu 16:15 Zelt West

**TrapRemi - A Device to Investigate the Quantum Dynamics of Molecular Ions** — ●FRANS SCHOTSCH, LUDWIG HOIBL, DENIS DJENDJUR, and ROBERT MOSHAMMER — Max-Planck-Institute for Nuclear Physics

The investigation of quantum few-body dynamics in atoms and molecules is of fundamental interest for physics and chemistry. Enabled by the innovation and development of Reaction Microscopes (REMI) during the last two decades, reactions such as ionization, dissociation and geometrical reformation can be investigated in an angle-resolved and kinematically complete manner. Combined with short-pulse laser systems, these dynamics can be even resolved on attosecond time scale. The TrapRemi extends this development to enable similar investigations in charged systems: atomic and molecular ions of arbitrary charge and mass. These systems are of high interest since they often play key roles in astrochemical reactions as for example the Trihydrogen cation. For this purpose, we designed a new experimental setup: The combination of a linear electrostatic ion trap (Zajfman-Trap) with a REMI. This poster describes the project progress from first ion optics simulations to successful ion storage.

MO 22.9 Thu 16:15 Zelt West

**molecular frame young-type interference in (e, 2e) reactions on hydrogen molecule** — ●ENLIANG WANG<sup>1</sup>, XUEGUANG REN<sup>1</sup>, KHOKON HOSSEN<sup>1</sup>, XINGYU LI<sup>2</sup>, XIANGJUN CHEN<sup>2</sup>, and ALEXANDER DORN<sup>1</sup> — <sup>1</sup>Max-Planck-Institut für Kernphysik, 69117 Heidelberg, Germany — <sup>2</sup>Hefei National Laboratory for Physical Sciences at Microscale and Department of Modern Physics, University of Science and Technology of China, Hefei, Anhui, 230026, China

The wave-particle duality is one of the fundamental concepts of quantum mechanism where the wave like behaviors of particles were mostly demonstrate through Young's double-slit experiment in which the coherent superposition of different outgoing amplitudes will present interference patterns. Here we perform a high energy ( $E_0 = 520$  eV) (e, 2e) experiment on H<sub>2</sub> to trace the interference effect using a dedicated reaction microscope. The present experimental results show that a strong dependence to the molecular alignment of the FDCE is observed where two intense areas are observed with molecular alignment at 0 and 180° for 10 eV ejected electrons. The MCDW calculation well reproduce the experimental results while the pure interference description fails completely. This is mainly due to the rather low energy (10 eV) of the ejected electron which does not justify the spherical wave description used in the derivation of the interference factor. Future experiments will consider fast outgoing electrons (up to 80 eV) to trace the interference effect.

MO 22.10 Thu 16:15 Zelt West

**Low-energy electron emission in strong-field photoionization of methane** — ●MARTIN LAUX, NICOLAS CAMUS, YONGHAO MI, LUTZ FECHNER, ROBERT MOSHAMMER, and THOMAS PFEIFER — Max-Planck-Institut für Kernphysik, Saupfercheckweg 1, 69117 Heidelberg, Germany

We present results of strong-field ionization of methane measured in a Reaction Microscope (Remi) by 25 fs, 800/400 nm two-color laser pulses. Photoelectron spectra were analyzed separately for different ionization and dissociation channels, which could be identified by the ion fragments detected in coincidence, i.e. CH<sub>4</sub><sup>+</sup>, CH<sub>3</sub><sup>+</sup>, and H<sup>+</sup>. The spectra differ significantly from each other at kinetic energies below 0.5 eV, in contradiction to the established two-step model of molecular

photoionization [1]. However, autoionization of vibrationally excited Rydberg states is found to explain the enhancement of low-energy electrons. Our findings generalize this strong-field excitation and autoionization mechanism, observed recently in molecular hydrogen [2], to more complex systems.

[1] M.F. Kling *et al.*, Science **312**, 246 (2006)

[2] Y. Mi *et al.*, Phys. Rev. Lett. **118**, 183201 (2017)

MO 22.11 Thu 16:15 Zelt West

**Fragmentation pathways of protonated nucleic acid building blocks** — ●MARTIN PITZER<sup>1,2</sup>, CHRISTIAN OZGA<sup>1</sup>, CATMARNA KÜSTNER-WETEKAM<sup>1</sup>, PHILIPP REISS<sup>1</sup>, ALEXANDRE GIULIANI<sup>3</sup>, and LAURENT NAHON<sup>3</sup> — <sup>1</sup>Institut für Physik und CINSaT, Universität Kassel, Germany — <sup>2</sup>Department of Chemical and Biological Physics, Weizmann Institute of Science, Rehovot, Israel — <sup>3</sup>Synchrotron SOLEIL, Gif-sur-Yvette, France

Ultraviolet radiation is known to have large absorption cross sections in biologically relevant molecules. Due to the complexity of these molecules, many destructive and non-destructive pathways for deexcitation exist. Which pathways are chosen is extremely relevant for the resulting radiation damage in biological tissue. Although not performed in a natural environment, experimental studies on isolated molecules are essential to understand the interplay between photoexcitation and fragmentation.

By combining an Electrospray Ionization source (ESI) with tunable photoexcitation in the VUV range and a tandem mass spectrometer, the appearance energies of fragments can be determined in dependence of various parameters such as hydration or charge state [1]. Our contribution shows recent results for the RNA components uracil and uridine which exhibit a rich fragmentation behaviour in the region of 4-12 eV photon energy. We compare for various fragments how the yield depends on the exciting photon energy and are thus able to test theoretically predicted fragmentation pathways and dissociation thresholds.

[1] A. Milosavljevic *et al.*, J. Synchrotron Rad. **19**, 174-178 (2012)

MO 22.12 Thu 16:15 Zelt West

**Laser Induced Electron Diffraction on strongly aligned OCS molecules** — ●PHILIPP M. STAMMER<sup>1</sup>, EVANGELOS THOMAS KARAMATSKOS<sup>2,3</sup>, SEBASTIAN RAABE<sup>1</sup>, GILDA GOLDSZTEJN<sup>1</sup>, ANDREA TRABATTONI<sup>2</sup>, TERENCE MULLINS<sup>2</sup>, SEBASTIAN TRIPPEL<sup>2,4</sup>, ARNAUD ROUZÉE<sup>1</sup>, and JOCHEN KÜPPER<sup>2,3,4</sup> — <sup>1</sup>Max Born Institute, Berlin, Germany — <sup>2</sup>DESY, Hamburg, Germany — <sup>3</sup>Universität Hamburg, Germany — <sup>4</sup>CUI, Hamburg, Germany

Strong Field Ionization of an atom or molecule is often described in a simple semi-classical picture: an electron is tunnel ionized by the intense laser field, accelerated away from the atom before to be driven back to the parent ion by the oscillating laser field. Elastic collision with the parent ion is responsible for the apparition of a second plateau in the photoelectron angular distribution that contains diffraction features from which one can extract direct information about the molecular geometry. This effect is used in a technique called Laser Induced Electron Diffraction (LIED).

To image ultrafast molecular dynamics Laser Induced Electron Diffraction has recently emerged as a powerful tool. We performed LIED experiments in strongly aligned OCS molecules and obtain photoelectron distributions for different angles of the laser polarizations with respect to the molecular orientation. The observed large modifications of the well-known holographic and fork structure with the alignment axis orientation will be discussed.

MO 22.13 Thu 16:15 Zelt West

**Vibrationally resolved electron-nuclear energy sharing in above-threshold multiphoton dissociation of CO** — ●XUFEI SUN — Max-Planck-Institut für Kernphysik, Saupfercheckweg 1, 69117 Heidelberg

We study the photon energy sharing between the photoelectron and the nuclei in the process of above-threshold multiphoton dissociative ionization of CO molecules by measuring the joint energy spectra. The experimental observation shows that the electron-nuclear energy sharing strongly depends on the vibrational state. The experimental observation shows that both the energy deposited to the nuclei of CO<sup>+</sup> and the emitted photoelectron decrease with increasing the vibrational level. Through studying the vibrationally resolved nuclear kinetic energy release and photoelectron energy spectra at different laser intensities, for each vibrational level of CO<sup>+</sup>, the nuclei always tend to take



the same amount of energy in every vibrational level regardless of the laser intensity, while the energy deposited to the photoelectron varies with respect to the laser intensity because of the ponderomotive shifted energy and the distinct dissociative ionization mechanisms.

MO 22.14 Thu 16:15 Zelt West

**Improved virtual orbitals for charge transfer excitations in time dependent DFT** — ●ROLF WÜRDEMANN<sup>1</sup> and MICHAEL WALTER<sup>2,3</sup> — <sup>1</sup>FMF, Universität Freiburg, Freiburg, Germany — <sup>2</sup>FIT, Universität Freiburg, Freiburg, Germany — <sup>3</sup>IWM, Freiburg, Germany

Charge transfer excitations (CTE) are of high importance in photo-voltics, organic electronics and molecular and organic magnetism. Range separated functionals (RSF) can be used to correctly determine the energetics of CTEs within linear response time dependent density functional theory (TDDFT).

TDDFT becomes numerically very demanding on grids if hybrid or RSF are used due to the inclusion of exact exchange derived from Hartree-Fock theory.

We present the implementation of RSF on real space grids and discuss a way to circumvent the problem mentioned above by utilizing Huzinagas improved virtual orbitals (IVOs) that form an improved basis for this type of calculations. The CTE energetics may be even obtained by means of DFT ground-state calculations using IVOs.

MO 22.15 Thu 16:15 Zelt West

**Predicting para-ortho conversion in ammonia** — ●GUANG YANG<sup>1</sup>, INGMAR HARTL<sup>2</sup>, ANDREY YACHMENEV<sup>1,3</sup>, and JOCHEN KÜPPER<sup>1,3,4</sup> — <sup>1</sup>Center for Free-Electron Laser Science, DESY, Notkestrasse 85, Hamburg — <sup>2</sup>DESY, Notkestrasse 85, Hamburg — <sup>3</sup>The Hamburg Center for Ultrafast Imaging, Luruper Chaussee 149, Hamburg — <sup>4</sup>Department of Physics, University of Hamburg, Luruper Chaussee 149, Hamburg

We present a theoretical study of the hyperfine-resolved spectrum of ammonia and its deuterated isotopologues in preparation of corresponding experiments. The calculations have been performed using variational approach TROVE, a new spectroscopically determined potential energy surface, and ab initio quadrupole, spin-spin, and spin-rotation coupling surfaces. The computed spectroscopic line lists cover transitions between levels with rotational excitations up to  $J = 20$  and vibrational band centers up to 8000 cm<sup>-1</sup> above zero point energy. Comparisons with experimental data confirm the high accuracy of the computed results. The perspectives of spectroscopic observation of the para-ortho interconversion, for instance using infrared frequency comb spectroscopy, and its modulation by external electric field are discussed.

MO 22.16 Thu 16:15 Zelt West

**Coupling of the  $2^2\Sigma^+$  and  $1^2\Pi$  of LiSr** — ●ERIK SCHWANKE, JULIA GERSCHMANN, HORST KNÖCKEL, SILKE OSPELKAUS, and EBERHARD TIEMANN — QUEST und Inst. f. Quantenopik, Leibniz Universität Hannover

Building on our spectroscopic study of the  $2^2\Sigma^+ - 1^2\Sigma^+$  system of LiSr, we modeled perturbations in the thermal emission spectrum as coupling between the  $F_1$  and  $F_2$  levels of the  $2^2\Sigma^+$  state and the  $1^2\Pi_{1/2}$  and  $1^2\Pi_{3/2}$  states. The rotational and vibrational constants of the  $2^2\Sigma^+$  state were derived from the thermal emission spectrum and laser-induced fluorescence in the near infrared.

Several large perturbations of the rotational ladders of  $v' = 0$  and  $v' = 1$  allow to estimate the rotational and vibrational constants of the  $2^2\Pi$  state, while accompanying smaller perturbations hint at its spin-orbit coupling constant. A preliminary deperturbation of one of the larger instances led to more refined values for the rotational and vibrational constants of  $1^2\Pi$ , as well as a first estimate the coupling strength and the spin-rotation coupling in  $2^2\Sigma^+$ . Adding further perturbed states, a more global picture of the coupling constants and the  $1^2\Pi$  state will be derived.

We will report on the status of the investigations.

MO 22.17 Thu 16:15 Zelt West

**High-resolution spectroscopy of tritiated water and analysis of the  $2\nu_1$  mode of HTO** — ●JOHANNES MÜLLER<sup>1</sup>, MAGNUS SCHLÖSSER<sup>1</sup>, FRANK HASE<sup>2</sup>, NICOLAS ZIEGLER<sup>1</sup>, ROBIN GRÖSSE<sup>1</sup>, DAVID HILLESHEIMER<sup>1</sup>, and JOHANNES ORPHAL<sup>2</sup> — <sup>1</sup>Institute for Technical Physics, Tritium Laboratory Karlsruhe (TLK), Karlsruhe Institute of Technology, Germany — <sup>2</sup>Institute for Meteorology and Climate Research (IMK-ASF), Karlsruhe Institute of Technology, Ger-

many

By measuring vibrational and rotational states of tritiated water using high-resolution FTIR spectroscopy, one can obtain data to validate or restrict quantum mechanical models of small molecules at high precision, such as water. Whereas spectroscopy of the H<sub>2</sub>O, HDO and D<sub>2</sub>O isotopologues is easily feasible at high accuracy as there are no restrictions on the sample amount, tritiated water is much harder to grasp. Due to its radiotoxicity and radiochemical activity, handling of tritiated water and gaseous tritium is only possible in a handful facilities worldwide. Therefore, a joint venture between the TLK, providing the tritium and experience in handling it, and the IMK-ASF, providing the expertise in high-resolution FTIR spectroscopy, was formed. We will describe how tritiated water is produced in a tritium compatible optical cell and how the high-resolution spectrometry is performed. We focus on the analysis the  $2\nu_1$  mode in the ro-vibrational spectrum of HTO which has never been measured before. We present rotational and centrifugal distortion constants of HTO, which allow us to access the fundamental structure and dynamic of this fascinating molecule.

MO 22.18 Thu 16:15 Zelt West

**Absorption spectroscopy on KCa** — ●JULIA GERSCHMANN<sup>1</sup>, ERIK SCHWANKE<sup>1</sup>, HORST KNÖCKEL<sup>1</sup>, SILKE OSPELKAUS<sup>1</sup>, ASEN PASHOV<sup>2</sup>, and EBERHARD TIEMANN<sup>1</sup> — <sup>1</sup>QUEST und Inst. f. Quantenopik, Leibniz Universität Hannover — <sup>2</sup>Sofia Universität "St. Kliment Ohridski", Bulgarien

The combination of an alkaline and an alkaline earth atom leads to molecules with 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. Experimentally, not so much is known about the molecular electronic states.

In the past we were able to describe potential energy curves for the first two  $2^2\Sigma^+$  states via high resolution Fourier transform spectroscopy. We have used laser induced fluorescence to assign the quantum numbers up to  $N = 179$  of transitions from  $v' \leq 7$  to  $v'' \leq 10$ . The rovibrational spectrum can be described by fitted potential energy curves and the spin-rotation coupling.

Currently, based on ab initio calculations, we set up a laser absorption experiment in the visible region around 17000 cm<sup>-1</sup> to address higher  $2^2\Sigma^+$  and  $2^2\Pi$  states from the known ground state. There we expect low density of K<sub>2</sub> lines. Lines thus identified as belonging to KCa can then be used for further laser induced fluorescence experiments.

We will report on the status of the investigations.

MO 22.19 Thu 16:15 Zelt West

**Electronic structure investigations on mono- and binuclear transition metal complexes** — ●TATJANA WALL<sup>1</sup>, LOUIS OBERWEIS<sup>1</sup>, MARKO LEIST<sup>2</sup>, WERNER THIEL<sup>2</sup>, and MARKUS GERHARDS<sup>1</sup> — <sup>1</sup>TU Kaiserslautern, Physical Chemistry & Research Center Optimas, Erwin-Schrödinger-Str. 52, 67663 Kaiserslautern, Germany — <sup>2</sup>TU Kaiserslautern, Inorganic Chemistry, Erwin-Schrödinger-Str. 54, 67663 Kaiserslautern, Germany

Binuclear heterometallic complexes are of great interest in synthesis due to their catalytic activity e.g. for transfer hydrogenation or cross-coupling. Absorption and emission spectra of mono- and binuclear transition metal complexes based on bispyrimidine in solution are recorded to investigate their electronic structure. Furthermore the lifetimes of the excited states are determined by using the time correlated single photon counting (TCSPC) method. The results are compared with the pure bispyrimidine ligand and additionally a comparison with DFT calculations is performed. Here we represent the results for mono- and binuclear Ir and Pd containing complexes. For both types of complexes MLCT (Metal to Ligand Charge Transfer) and ligand centered transitions are observed. Lifetime determinations show multiple exponential decays for all emission bands, whereas the emission band of the pure ligand has a mono-exponential decay. The average lifetimes of the ligand centered bands are similar to the lifetime of the pure ligand. The photophysics of complexes with respect to lifetimes, coordination sites and characters of electronically excited states are discussed.

MO 22.20 Thu 16:15 Zelt West

**Ionization Loss/Gain Stimulated Raman Spectroscopy of isolated molecules in the gas phase: diphenyl ether and bisphenyldiamantane** — ●DOMINIQUE MAUE<sup>1</sup>, ANKE STAMM<sup>1</sup>, DOMINIC BERNHARD<sup>1</sup>, ANDREY FOKIN<sup>2</sup>, PETER SCHREINER<sup>2</sup> und MARKUS GERHARDS<sup>1</sup> — <sup>1</sup>TU Kaiserslautern, Department of Chemistry,



Physical Chemistry, Erwin-Schrödinger-Str. 52, 67663 Kaiserslautern, Germany — <sup>2</sup>Universität Gießen, Department of Chemistry, Organic Chemistry, Heinrich-Buff-Ring 17, 35392 Gießen, Germany

Ionization Loss/Gain Stimulated Raman Spectroscopy (ILSRS/ILGRS) is a powerful tool for the structural investigation of isolated molecules and clusters in the gas phase. With these methods, it is possible to investigate structurally relevant Raman active vibrations as well as the spectral range below 800  $\text{cm}^{-1}$ , which is

difficult to access with table top IR lasers in molecular beam experiments. Here, we present the first examinations with the newly installed ILSRS/ILGRS setup investigating diphenyl ether (DPE) and bisphenyldiamantane (BPA) in the gas phase. This is the first application of the stimulated Raman technique on the class of diadamantanes, which is of great importance because of the extraordinary length of the connective C-C bond. In combination with dispersion-corrected DFT calculations we are able to receive a structural agreement of experiment and theory.

## MO 23: Resonant Energy Transfer and Interatomic Coulombic Decay II

Time: Friday 10:30–12:00

Location: PA 1.150

MO 23.1 Fri 10:30 PA 1.150

**Intermolecular decay mechanisms in pure and doped helium nanodroplets** — ●AARON LAFORGE<sup>1</sup>, RUPERT MICHIELS<sup>1</sup>, CARLO CALLEGARI<sup>2</sup>, MICHELE DI FRAIA<sup>2</sup>, MARCEL DRABELLS<sup>3</sup>, BRUNO LANGBEHN<sup>4</sup>, MARCEL MUDRICH<sup>5</sup>, VERONICA OLIVER<sup>3</sup>, YEVHENY OVCHARENKO<sup>4</sup>, OKSANA PLEKAN<sup>2</sup>, KEVIN PRINCE<sup>2</sup>, THOMAS MÖLLER<sup>4</sup>, and FRANK STIENKEMEIER<sup>1</sup> — <sup>1</sup>Universität Freiburg, Germany — <sup>2</sup>Elettra-Sincrotrone Trieste, Italy — <sup>3</sup>EPFL Lausanne, Switzerland — <sup>4</sup>TU Berlin Germany — <sup>5</sup>Aarhus University, Denmark

As opposed to molecular systems where electron dynamics proceed only through intramolecular processes, weakly bound complexes create an environment in which locally excited electrons can additionally interact with neighboring molecules leading to new intermolecular decay mechanisms. Here, we present a systematic study of intermolecular decay mechanisms in pure and doped He nanodroplets using free electron laser radiation. When resonantly excited, the nanodroplets can either exchange energy with neighboring He atoms or through the acceptor dopants. By pump-probe techniques combined with photoelectron spectroscopy, we can fully characterize and energetically resolve the different decay paths.

MO 23.2 Fri 10:45 PA 1.150

**Time-Resolved Interatomic Coulomb Electron-Capture by Ba<sup>+</sup> through Rb proximity** — ●AXEL MOLLE<sup>1</sup>, ORIOL VENDRELL<sup>2</sup>, and ANNIKA BANDE<sup>1</sup> — <sup>1</sup>Institute for Methods for Material Development, Helmholtz-Zentrum Berlin f. Materialien & Energie, Berlin — <sup>2</sup>Department of Physics and Astronomy, Aarhus University, Aarhus, Denmark

In this work, we will present results of a time-resolved numerical investigation of the Ultrafast Interatomic Coulomb Electron Capture (ICEC) as a first attempt to predict experiments of the near future. A species *A* captures a free electron in the ICEC process by long-range energy transfer through Coulomb interaction to a bound electron in a neighbouring species *B*, which is then ionized.

From a theoretical perspective, even though first predicted for atoms and molecules through the asymptotic approximation of scattering theory [1], investigation of the time-resolved ICEC dynamics has been successful in lower-dimensional systems [2]. From the experimental side, on the other hand, techniques for trapping ultracold ions and atom clouds are advancing. This may enable investigating ICEC in an experiment in the near future.

We thus numerically study the dynamics of such an exemplary experiment at ultracold temperatures, with a barium cation trapped in a cloud of rubidium atoms, in order to predict and pave the way for time-resolved ICEC experiments.

[1] Gokhberg / Cederbaum, Phys. Rev. A **82** (2010).

[2] Pont *et al.*, J. Phys. Condens. Matter **28** (2016).

MO 23.3 Fri 11:00 PA 1.150

**Evidence for direct detection of radiative charge transfer photons from Auger final states in neon clusters** — ●ANDREAS HANS<sup>1</sup>, VASIL STUMPF<sup>2</sup>, XAVER HOLZAPFEL<sup>1</sup>, PHILIPP SCHMIDT<sup>1</sup>, CHRISTIAN OZGA<sup>1</sup>, CATMARNA KÜSTNER-WETEKAM<sup>1</sup>, TILL JAHNKE<sup>3</sup>, ARNO EHRESMANN<sup>1</sup>, PHILIPP V. DEMEKHIN<sup>1</sup>, KIRILL GOKHBERG<sup>2</sup>, and ANDRÉ KNIE<sup>1</sup> — <sup>1</sup>Institut für Physik und CINSaT, Universität Kassel, Heinrich-Plett-Str. 40, 34132 Kassel, Germany — <sup>2</sup>Physikalisch-Chemisches Institut, Universität Heidelberg, Im Neuenheimer Feld 229, 69120 Heidelberg, Germany — <sup>3</sup>Institut für Kernphysik, Goethe-Universität, Max-von-Laue-Str. 1, 60438 Frankfurt, Germany

Non-local charge distribution processes in dense samples like clusters and liquids have recently attracted tremendous attention in atomic and molecular physics. As a result of progress in both theory and experiment a variety of mechanisms was predicted and observed. Among them is radiative charge transfer (RCT), in which the transfer of an electron from a neutral site of a cluster to a doubly charged site is accompanied by photon emission. The occurrence of RCT has been experimentally deduced from energy conservation reasons by multi-particle coincidence detection after inner-shell ionization and subsequent Auger decay in noble gas clusters. However, direct observation of the emitted photons has not been reported so far, although this might be an advantageous method to track RCT in dense matter. Here, we report evidence for the first measurement of photons emitted in an RCT process in large neon clusters.

MO 23.4 Fri 11:15 PA 1.150

**Ultrafast intermolecular relaxation process in hydrated biomolecule cluster** — ●XUEGUANG REN, ENLIANG WANG, KHOKON HOSSEN, and ALEXANDER DORN — Max-Planck-Institut für Kernphysik, 69117 Heidelberg, Germany

It is accepted that DNA lesions are induced by secondary species like radicals and the abundant low-energy secondary electrons generated by the primary radiation. In the present work we report the observation of hitherto unrecognized damage mechanism in form of a non-local autoionizing process called intermolecular coulombic decay (ICD) which directly ionizes DNA constituents in an aqueous environment. As a model system hydrogen-bonded dimers are used which consist of one tetrahydrofuran (THF) molecule - a surrogate of deoxyribose in the DNA backbone - and one water molecule. After inner-valence ionization of water by electron impact the vacancy is filled by an electron from an outer-valence orbital and ultrafast energy transfer across the hydrogen bridge leads to ionization of the neighboring THF molecule and ejection of an electron. This energy transfer from water to THF is faster than the otherwise occurring intermolecular proton transfer. The signature of the ICD reaction is identified in triple coincidence measurements of both ions and one of the final state electrons.

MO 23.5 Fri 11:30 PA 1.150

**Approaches to the Interatomic Coulombic Decay in neutral quantum dots** — ●MARTIN LÜTZNER and ANNIKA BANDE — Helmholtz-Zentrum Berlin für Materialien und Energie, Hahn-Meitner Platz 1, 14109 Berlin, Germany

The interatomic Coulomb decay (ICD) is an ultrafast, radiationless energy transfer process between atoms and molecules. In ICD an electron in an innervalence state of an atom deexcites by transferring energy to an electron in another atom. This causes the second electron to leave the neighbouring atom if the excitation energy of the first atom lies above the ionization threshold of the second one. Recent theoretical investigations predicted ICD happening in a system of two neighbouring charged semiconductor Quantum Dots (QD).

In the current description of charged QDs electronically excited intraband states were considered. Since excitonic states are more long-lived and play a major role in the optical properties of semiconductors, it is desirable to describe neutral quantum dots. In this talk an approach on the description of ICD in neutral QDs will be given. The holes in this model are regarded as static pointlike particles. Furthermore the effects of Coulomb screening on the carrier dynamics is investigated.

MO 23.6 Fri 11:45 PA 1.150

**Interatomic Coulombic Decay in Real-Life** — ●ROBERT

BENNETT<sup>1</sup>, JOSHUA LEO HEMMERICH<sup>1</sup>, and STEFAN YOSHI BUHMANN<sup>1,2</sup> — <sup>1</sup>University of Freiburg, Germany — <sup>2</sup>Freiburg Institute for Advanced Studies (FRIAS), Freiburg, Germany

Interatomic Coulombic decay (ICD) is a mechanism by which energy can be very rapidly redistributed between molecular systems. The ICD process includes production of a free electron, which is normally of relatively low energy. These ‘slow’ electrons can cause damage to biological systems, in particular to DNA. Biological processes of course take place outside the idealised conditions studied so far in ICD, rather

proceeding in non-trivial environments such as those found in solvent media, near a cell membrane or in a molecular chain.

In this talk I will present a newly-developed theory of ICD based on macroscopic quantum electrodynamics in media that naturally takes into account the effects of the environment, as well as those of relativistic retardation. It will be shown that orders-of-magnitude enhancement of the rate can be missed by ignoring retardation, and that the rate can be significantly enhanced or suppressed depending on the orientation of the decaying system relative to a nearby surface.

## MO 24: Experimental Techniques

Time: Friday 10:30–12:15

Location: PA 2.150

MO 24.1 Fri 10:30 PA 2.150

**Investigations of Molecular Dynamics using Gas-Phase Ultrafast Electron Diffraction** — THOMAS WOLF<sup>1,2</sup>, JIE YANG<sup>1</sup>, ●MATTHEW S. ROBINSON<sup>3</sup>, J. PEDRO F. NUNES<sup>4</sup>, THEODORE VECCHIONE<sup>1</sup>, RENAKI LI<sup>1</sup>, NICK HARTMANN<sup>1</sup>, XIAOZHE SHEN<sup>1</sup>, RYAN COFFEE<sup>1</sup>, JEFF CORBETT<sup>1</sup>, JAMES CRYAN<sup>1,2</sup>, ALAN FRY<sup>1</sup>, KELLY GAFFNEY<sup>1</sup>, TAIS GORKHOVER<sup>1</sup>, KARSTEN HAST<sup>1</sup>, KAREEM HEGAZY<sup>1</sup>, KEITH JOBE<sup>1</sup>, IGOR MAKASYUK<sup>1</sup>, ALEXANDER REID<sup>1</sup>, JOSEPH ROBINSON<sup>1</sup>, SHARON VETTER<sup>1</sup>, FENGLIN WANG<sup>1</sup>, STEPHEN WEATHERSBY<sup>1</sup>, KYLE WILKIN<sup>5</sup>, CHARLES YONEDA<sup>1</sup>, QIANG ZEHNG<sup>1</sup>, MARTIN CENTURION<sup>5</sup>, MARKUS GÜHR<sup>1,2,3</sup>, and XIJIE WANG<sup>1</sup> — <sup>1</sup>SLAC, Menlo Park, USA — <sup>2</sup>PULSE, Menlo Park, USA — <sup>3</sup>Physik und Astronomie, Potsdam, Germany — <sup>4</sup>Chemistry, York, UK — <sup>5</sup>Physics and Astronomy, Lincoln-Ne, USA.

With its ability to provide direct structural information of molecules and how they change in an excited state, Ultrafast Electron Diffraction (UED) is becoming one of the most useful techniques in ultrafast science.[1] At the forefront of this are the MeV gas-phase UED experiments carried out at SLAC, which have observed molecular wavepackets using diffraction methods with unprecedented sub-Ångstrom spatial, and 100 fs temporal, resolution.[2,3] In this talk I will discuss several UED experiments, including the study of N<sub>2</sub> rotational wavepackets, I<sub>2</sub> vibrational wavepackets, and the recent investigation of the ring-opening process of stilbene oxide. 1 - Sciaini, G. et al. Rep. Prog. Phys. 74, 96101, 2011. 2 - Yang, J. et al., Nat. Commun. 7, 11232, 2016. 3 - Yang, J. et al., Phys. Rev. Lett. 117, 153002, 2016.

MO 24.2 Fri 10:45 PA 2.150

**Electronic wave packet interferometry in the UV - first steps towards coherent time-domain XUV spectroscopy** — ●ANDREAS WITUSCHEK<sup>1</sup>, LUKAS BRUDER<sup>1</sup>, ULRICH BANGERT<sup>1</sup>, MARCEL BINZ<sup>1</sup>, LARS-STEPHAN KLEIN<sup>1</sup>, TIM LAARMANN<sup>2,3</sup>, and FRANK STIENKEMEIER<sup>1</sup> — <sup>1</sup>Universität Freiburg, Physikalisches Institut, Hermann-Herder-Str. 3, 79104 Freiburg, Germany — <sup>2</sup>Deutsches Elektronen-Synchrotron DESY, Notkestr. 85, 22607 Hamburg, Germany — <sup>3</sup>The Hamburg Centre for Ultrafast Imaging CUI, Luruper Chaussee 149, 22761 Hamburg, Germany

Coherent time-resolved spectroscopy is a powerful tool to study ultrafast dynamics in complex systems. Extending this to the XUV spectral region is on the frontier of nonlinear spectroscopy. However, demands on interferometric stability increase when going to short wavelengths and advanced pulse manipulation in the XUV is challenging. In seeded free electron lasers (FEL) the emitted XUV pulses inherit the coherence properties of the seed pulses [1]. This motivates our approach based on a stable and transportable platform performing acousto-optical phase modulation on the seed laser with subsequent seeding of the FEL and lock-in detection at the harmonics of the seed modulation [2]. This reduces demands on interferometric stability and signals are efficiently isolated and amplified [3]. The platform has been characterized on dilute sodium vapor, which allowed us to record electronic quantum beats at 268nm.

[1] Gauthier et al., PRL 116, 024801 (2016), [2] Bruder et al., Opt. Express 25, 5302-5315 (2017), [3] Bruder et al., PRA 92, 053412 (2015)

MO 24.3 Fri 11:00 PA 2.150

**Electron cooling of bunched ion beams and experimental program of the CSR electron merged beam setup** — ●PATRICK WILHELM, ARNO BECKER, CLAUDE KRANTZ, JORRIT LION, SVENJA LOHMANN, OLDŘICH NOVOTNÝ, MARIUS RIMMLER, SUNNY SAURABH, STEPHEN VOGEL, and ANDREAS WOLF — Max Planck Institute for

Nuclear Physics, Heidelberg, Germany

In the Cryogenic Storage Ring (CSR) molecular ions are stored for hundreds to thousands of seconds in a low-temperature radiation field given by the black-body radiation of the beamline wall at less than 10 K. By this stored molecular and cluster ions can undergo radiative relaxation toward their ro-vibrational ground-state. Measurements probing fundamental molecular and cluster dynamics can be performed with good internal state definition. For ion-beam phase-space cooling a low-energy electron cooler was set up for the CSR. Cold electrons are produced by a LN<sub>2</sub>-cooled GaAs photocathode. Merging of the electrons with the stored ion beam is realized by a magnetic guiding field which is created by a set of high-temperature superconducting solenoids, toroids and racetrack coils. The CSR electron cooler is designed to achieve an average kinetic electron-beam energy as low as 1 eV at a rest-frame energy spread of about 1 meV. It was successfully taken into operation in June 2017. A ~40 eV electron beam was merged with a 1200 keV F<sup>6+</sup> ion beam and bunched-beam electron cooling has been demonstrated. Upcoming beamtimes will aim at phase-space cooling and high-resolution studies of electron-ion reactions.

MO 24.4 Fri 11:15 PA 2.150

**Optimization of field-free alignment of molecules for imaging experiments** — ●EVANGELOS THOMAS KARAMATSKOS<sup>1,2</sup>, SEBASTIAN RAABE<sup>3</sup>, PHILIPP STAMMER<sup>3</sup>, ANDREA TRABATTONI<sup>1</sup>, TERENCE MULLINS<sup>1</sup>, GILDAS GOLDSZTEJN<sup>3</sup>, SEBASTIAN TRIPPEL<sup>1,4</sup>, ARNAUD ROUZÉE<sup>3</sup>, and JOCHEN KÜPPER<sup>1,2,4,5</sup> — <sup>1</sup>CFEL, DESY, Hamburg, Germany — <sup>2</sup>Department of Physics, Universität Hamburg, Germany — <sup>3</sup>Max-Born Institute, Berlin, Germany — <sup>4</sup>CUI, Universität Hamburg, Germany — <sup>5</sup>Department of Chemistry, Universität Hamburg, Germany

Field-free alignment and orientation of molecules is an important prerequisite for many gas phase imaging experiments. It allows to access information directly in the molecular frame and extract observables such as internuclear distances, angles and the electronic density through a measurement of the photoelectron angular distribution. We present new experimental results and simulations on strongly field-free aligned molecules, ranging from linear to complex asymmetric rotor molecules. Additionally, photoelectron momentum distributions of strongly aligned OCS molecules, recorded experimentally at different angles between the laser polarization axis and the molecular axis will be presented. The photoelectron angular distributions display large modifications with the molecular axis distribution, both at low and high kinetic energies, which encode the molecular structure and electronic density of the molecule. A discussion of the experimental results will be presented.

MO 24.5 Fri 11:30 PA 2.150

**Coherent anti-stokes Raman spectroscopy in gas-filled hollow-core PCF** — ●RINAT TYUMENEV<sup>1</sup>, BARBARA TRABOLD<sup>1</sup>, AMIR ABDOLVAND<sup>2</sup>, LUISA SPAETH<sup>1</sup>, and PHILIP ST J RUSSEL<sup>1</sup> — <sup>1</sup>Max-Planck-Institut für die Physik des Lichts Stadtstraße 2 91058 Erlangen — <sup>2</sup>Nanyang Technological University

Gas sensing and composition analysis are of great importance in numerous fields, for example environmental studies of greenhouse gases and toxic substances, medicine for detection of marker gases in human breath, chemical and industrial applications. Raman spectroscopy provides quantitative molecule-specific measurement of analytes. However, some analytes, for example gases, have relatively weak Raman gain and at low concentrations free space Raman spectroscopy yields

tiny signal levels, which require very powerful pump lasers to be detectable. We present an approach that relaxes the need for high laser power and provides broadband Raman spectroscopy of gas mixtures. The approach is based on coherent anti-Stokes Raman spectroscopy in gas filled hollow-core photonic crystal fibre (PCF). The hollow core provides long interaction lengths allied to core diameters of a few tens of micrometers, dramatically increasing the CARS signal. The ability to change the dispersion of the waveguide by altering the gas pressure or (less practically) the PCF geometry permits CARS phase-matching over a broad wavelength range, so that the Raman signal can build up coherently over the whole fiber length. We report broadband (4000 1/cm) single-shot CARS with a concentration detection limit of 300 ppm.

MO 24.6 Fri 11:45 PA 2.150

**Generation, Shaping, and Complete Characterization of Complex Mid-Infrared-fs Laser Pulses** — ●MARKUS ALEXANDER JAKOB<sup>1,2</sup>, MARK PRANDOLINI<sup>3</sup>, ROBERT RIEDEL<sup>4</sup>, GIULIO MARIA ROSSI<sup>2,5</sup>, MICHAEL SCHULZ<sup>4</sup>, and TIM LAARMANN<sup>1,2</sup> — <sup>1</sup>The Hamburg Centre for Ultrafast Imaging, Universität Hamburg, 22761 Hamburg — <sup>2</sup>Deutsches Elektronen-Synchrotron, 22607 Hamburg — <sup>3</sup>Institut für Experimentalphysik, Universität Hamburg — <sup>4</sup>Class 5 Photonics GmbH, 22607 Hamburg — <sup>5</sup>Center for Free-Electron Laser Science, 22607 Hamburg

Shape-optimized Mid-IR laser pulses at a central wavelength of around 10  $\mu\text{m}$  represent a genuine tool to study coupling of different vibrational modes in complex molecular systems, as well as to manipulate charge and energy transport mechanisms and might even be used to influence catalytic behaviour. A scheme will be presented, that enables for generation of wavelength tunable and CEP stable Mid-IR laser pulses, their arbitrary shaping by means of an acousto-optical

modulator, and their full characterization. These provide an excellent toolbox to address specific vibrational modes in large molecular systems and to influence and steer associated dynamics in the electronic ground state. This is where chemistry typically takes place.

MO 24.7 Fri 12:00 PA 2.150

**Molecular frame 3D momentum imaged using TimePix3** — ●RUTH LIVINGSTONE<sup>1</sup>, MILIJA SARAJLIC<sup>2</sup>, DAVID PENNICARD<sup>2</sup>, MARTIN VAN BEUZEKOM<sup>3</sup>, BAS VAN DER HEIJDEN<sup>3</sup>, JAN VISSER<sup>3</sup>, HEINZ GRAAFSMA<sup>2</sup>, ANDREI NOMEROTSKI<sup>4</sup>, SEBASTIAN TRIPPEL<sup>1,2</sup>, and JOCHEN KÜPPER<sup>1,2,5</sup> — <sup>1</sup>The Hamburg Center for Ultrafast Imaging, Luruper Chaussee 149, Universität Hamburg, DE — <sup>2</sup>Hamburg Center for Free-Electron Laser Science, DESY, Notkestrasse 85, DE — <sup>3</sup>National Institute of Subatomic Physics NIKHEF, Science Park 105, Amsterdam, NL — <sup>4</sup>Brookhaven National Laboratory, Upton, NY, USA — <sup>5</sup>Department of Physics & Department of Chemistry, Universität Hamburg, DE

Timepix3 is a powerful new detector for imaging photons, ions, or electrons with 1.8 ns time resolution [1]. Here, we demonstrate the capabilities of the detector by measuring carbonyl sulphide (OCS) fragment momentum vectors after strong field ionization. The full 3D momenta of the  $\text{OCS}^{++} \rightarrow \text{OC}^{++} + \text{S}^{+}$  fragmentation channel were measured in coincidence mode, allowing for the molecular frame distribution to be reconstructed. The Timepix detector was integrated into the current spectrometer setup without modification to the vacuum chamber. The resulting temporal resolution was under 3 ns, as a result of the phosphor used. The advantages of this detector over the current time resolved detection methods will be discussed, along with ways to achieve the optimum temporal resolution.

[1] A. Zhao et. al., Rev. Sci. Instrum. 88, 113104 (2017)