

Molecular Physics Division Fachverband Molekülphysik (MO)

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Overview of Invited Talks and Sessions

(Lecture rooms S HS 001 Biologie and S HS 002 Biologie; Poster S Foyer LLM)

Invited Talks

MO 3.1	Mon	10:30–11:00	S HS 001 Biologie	Solvent-Specific Facets in the Ultrafast Photochemistry of Reactive Intermediates — JOHANNES KNORR, PANDIAN SOKKAR, SVENJA WORTMANN, PAOLO COSTA, NIKLAS GESSNER, JULIEN ROWEN, WOLFRAM SANDER, ELSA SANCHEZ-GARCIA, ●PATRICK NUERNBERGER
MO 4.1	Mon	10:30–11:00	S HS 002 Biologie	Determination of Excited State Dipole Moments for Complex Systems - From Gas to the Condensed Phase — ●MICHAEL SCHMITT, MARIE-LUISE HEBESTREIT, MIRKO LINDIC, MATTHIAS ZAJONZ, MICHAEL SCHNEIDER
MO 6.1	Mon	14:00–14:30	S HS 001 Biologie	Investigation of structures and electronic states of transition metal containing complexes <i>via</i> transient FTIR spectroscopy — PATRICK DI MARTINO-FUMO, PIT BODEN, JASMIN BUSCH, SVEN OTTO, KATJA HEINZE, STEFAN BRÄSE, ●MARKUS GERHARDS
MO 11.1	Wed	10:30–11:00	S HS 001 Biologie	Properties of multiazobenzene systems - old dogs and new tricks — ●CHAVDAR SLAVOV, CHONG YANG, LUCA SCHWEIGHAUSER, ANDREAS H. HEINDL, TIM STAUCH, HERMANN A. WEGNER, ANDREAS DREUW, JOSEF WACHTVEITL
MO 19.1	Thu	10:30–11:00	S HS 001 Biologie	Optical spectroscopy of small metal clusters: a deeper look at Au₄⁺ — ●MARKO FÖRSTEL, WOLFGANG SCHEWE, OTTO DOPFER
MO 21.1	Thu	14:00–14:30	S HS 001 Biologie	Influence of Local and External Electric Fields on the Ultrafast Dynamics of Charge Pairs Photo-Generated in Poly-[3-Hexylthiophene] (P3HT) — DEBKUMAR RANA, TAHIRZEB KHAN, PATRICE DONFACK, VLADISLAV JOVANOV, VEIT WAGNER, ●ARNULF MATERNY
MO 23.1	Fri	10:30–11:00	S HS 001 Biologie	Efficient charge transfer by electron transfer mediated decay mechanism — ●KIRILL GOKHBERG

Invited talks of the joint symposium SYPS

See SYPS for the full program of the symposium.

SYPS 1.1	Mon	14:00–14:30	U Audimax	Optimal control of many-body quantum systems — ●SIMONE MONTANGERO
SYPS 1.2	Mon	14:30–15:00	U Audimax	Light matter quantum interface based on single colour centres in diamond — ●FEDOR JELEZKO
SYPS 1.3	Mon	15:00–15:30	U Audimax	Principles of Quantum Systems Theory and Control Engineering — ●THOMAS SCHULTE-HERBRÜGGEN
SYPS 1.4	Mon	15:30–16:00	U Audimax	Quantum metrology with Rydberg atoms — ●SEBASTIEN GLEYZES, ARTHUR LARROUY, REMI RICHAUD, SABRINA PATSCH, JEAN-MICHEL RAIMOND, MICHEL BRUNE, CHRISTIANE KOCH

Invited talks of the joint symposium SYAD

See SYAD for the full program of the symposium.

SYAD 1.1	Tue	10:30–11:00	U Audimax	Quantum States and their Marginals: from Multipartite Entanglement to Quantum Error-Correcting Codes — ●FELIX HUBER
SYAD 1.2	Tue	11:00–11:30	U Audimax	The Uniform Electron Gas at Warm Dense Matter Conditions — ●SIMON GROTH
SYAD 1.3	Tue	11:30–12:00	U Audimax	Relativistically intense laser-microplasma interactions (and potential applications) — ●TOBIAS OSTERMAYER
SYAD 1.4	Tue	12:00–12:30	U Audimax	Motional quantum state engineering for quantum logic spectroscopy of molecular ions — ●FABIAN WOLF

Invited talks of the joint symposium SYXR

See SYXR for the full program of the symposium.

SYXR 1.1	Thu	14:00–14:30	U Audimax	Superradiance of an ensemble of nuclei excited by a free electron laser — ●ALEKSANDR CHUMAKOV
SYXR 1.2	Thu	14:30–15:00	U Audimax	Quantum imaging with incoherently scattered light from a Free-Electron Laser — ●JOACHIM VON ZANTHIER
SYXR 1.3	Thu	15:00–15:30	U Audimax	Stimulated X-Ray Emission Spectroscopy for Chemical Analysis — ●NINA ROHRINGER
SYXR 1.4	Thu	15:30–16:00	U Audimax	X-Ray Multiphoton Ionization of Atoms and Molecules — ●DANIEL ROLLES

Sessions

MO 1.1–1.2	Sun	16:00–18:00	U HS 224	Tutorial Molecular Spectroscopy (joint session AKjDPG/MO)
MO 2.1–2.7	Mon	10:30–12:15	S HS 1 Physik	Ultra-cold atoms and molecules I (joint session A/MO/Q)
MO 3.1–3.7	Mon	10:30–12:30	S HS 001 Biologie	Ultrafast Processes in Solution
MO 4.1–4.7	Mon	10:30–12:30	S HS 002 Biologie	Electronic Spectroscopy
MO 5.1–5.8	Mon	14:00–16:00	S HS 1 Physik	Ultra-cold atoms and molecules II (joint session A/MO/Q)
MO 6.1–6.7	Mon	14:00–16:00	S HS 001 Biologie	Metal Complexes
MO 7.1–7.8	Mon	14:00–16:00	S HS 002 Biologie	Experimental Techniques
MO 8.1–8.6	Mon	16:15–17:45	S HS 001 Biologie	XUV and X-ray Excitation and Spectroscopy
MO 9.1–9.6	Mon	16:15–17:45	S HS 002 Biologie	Molecules in Intense Laser Fields
MO 10.1–10.20	Tue	16:30–18:30	S Foyer LLM	Posters 1: Cold Molecules, High Resolution Spectroscopy, and Theory
MO 11.1–11.7	Wed	10:30–12:30	S HS 001 Biologie	Photochemistry
MO 12.1–12.8	Wed	10:30–12:30	S HS 002 Biologie	High Resolution Spectroscopy and Precision Experiments
MO 13	Wed	12:45–13:45	S HS 001 Biologie	Annual General Meeting of the Molecular Physics Division
MO 14.1–14.8	Wed	14:00–16:00	S HS 001 Biologie	Ultrafast Multidimensional and Control Approaches
MO 15.1–15.8	Wed	14:00–16:00	S HS 002 Biologie	Cold Molecules (joint session MO/A)
MO 16.1–16.7	Wed	14:00–16:15	S HS 3 Physik	Cluster I (joint session A/MO)
MO 17.1–17.10	Wed	16:15–18:15	S Fobau Physik	Cluster II (joint session A/MO)
MO 18.1–18.20	Wed	16:15–18:15	S Foyer LLM	Posters 2: Time Resolved Spectroscopy
MO 19.1–19.7	Thu	10:30–12:30	S HS 001 Biologie	Cluster III (joint session MO/A)
MO 20.1–20.8	Thu	10:30–12:30	S HS 002 Biologie	Atomic Physics, Molecular Physics, and Quantum Optics with X-ray FELs (joint session MO/A)
MO 21.1–21.7	Thu	14:00–16:00	S HS 001 Biologie	Coupled Systems
MO 22.1–22.20	Thu	16:15–18:15	S Foyer LLM	Posters 3: Cluster, Strong Field Physics, and Experimental Techniques
MO 23.1–23.7	Fri	10:30–12:30	S HS 001 Biologie	Molecular Theory
MO 24.1–24.8	Fri	10:30–12:30	S HS 002 Biologie	Large and Reactive Systems

Annual General Meeting of the Molecular Physics Division

Wednesday 12:45–13:45 S HS 001 Biologie

MO 1: Tutorial Molecular Spectroscopy (joint session AKJDPG/MO)

Time: Sunday 16:00–18:00

Location: U HS 224

Tutorial MO 1.1 Sun 16:00 U HS 224
How Ultrafast Spectroscopy Can Follow Molecular Reaction Dynamics in Real Time — ●PATRICK NUERNBERGER — Physikalisches Chemie II, Ruhr-Universität Bochum, 44780 Bochum

Physicists and chemists are usually very familiar with absorption spectrometers. The obtained spectra provide information on energy levels and further properties of the substance at hand. Whereas one directly determines which photon is absorbed and how well, some of the most interesting information is not accessible in this way: what happens directly *after* the photon has interacted with the molecules?

Quite intuitively, one needs to measure at a later time to find out. Instead of looking only at the reaction's start and finish, a comprehensive approach has to follow the dynamics in real time in order to identify intermediates and decipher the underlying reaction mechanisms. For this, laser pulses in the femtosecond range are required, since photophysical processes and photochemical reactions (where bonds are cleaved and formed) may occur on an ultrafast time scale.

In this tutorial, the basics of ultrafast molecular spectroscopy are introduced. Different experimental implementations and the applicability to systems ranging from diatomic molecules to large biosystems are discussed. Two versatile approaches, transient absorption and coherent two-dimensional spectroscopy, are analyzed in detail with illustrative examples.

Tutorial MO 1.2 Sun 17:00 U HS 224

Theoretical Perspective on Time-resolved Spectroscopy of Molecular Systems — ●OLIVER KÜHN — University of Rostock, Institute of Physics, 18059 Rostock, Germany

Experiments in ultrafast spectroscopy have advanced to an unprecedented level of sophistication, being able to unravel even the finest details of molecular dynamics. Applications range from gas phase dynamics to the initial steps of photosynthesis, thereby encompassing many orders of magnitude as far as time and frequency scales are concerned. The analysis and interpretation requires advanced theoretical methods that can cope with the challenges provided by the experimental data. Here, ideas from electronic structure theory and quantum dynamics meet, areas which evolved separately so far.

In this tutorial, basic concepts of theoretical time-resolved spectroscopy will be discussed using applications from recent literature. In particular it will be shown that in the weak-field limit a rigorous and practical formulation of (non-)linear signals in terms of multi-time response functions can be given. Their information content is fully explored within two-dimensional spectroscopies, which have been developed to probe vibrational as well as electronic excitation dynamics.

[1] V. May and O. Kühn, *Charge and Energy Transfer Dynamics in Molecular Systems*, Wiley-VCH, 2011; [2] P. Hamm and M. T. Zanni, *Concepts and Methods of 2D Infrared Spectroscopy*, Cambridge, 2011; [3] M. Schröter, S. D. Ivanov, J. Schulze, S. P. Polyutov, Y. Yan, T. Pullerits, O. Kühn, *Phys. Rep.* 567, 1 (2015).

MO 2: Ultra-cold atoms and molecules I (joint session A/MO/Q)

Time: Monday 10:30–12:15

Location: S HS 1 Physik

MO 2.1 Mon 10:30 S HS 1 Physik
Quantum state-dependent reactive collisions of OH⁻ with ultracold Rubidium in a hybrid trap — ●SABA ZIA HASSAN¹, JONAS TAUCH¹, ERIC ENDRES¹, MARKUS NÖTZOLD², HENRY LOPEZ¹, BASTIAN HÖLTKEMEIER¹, ROLAND WESTER², and MATTHIAS WEIDEMÜLLER¹ — ¹Physikalisches Institut Heidelberg, INF 226, 69120 Heidelberg — ²Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck, 6020 Innsbruck

The study of ion-molecule reactions plays a vital role in cold chemistry, implying the need of well-controlled ion ensembles in a cold environment. The internal and external degrees of freedom of molecular ions, trapped in multipole radio frequency ion traps, can be cooled via collisions, with pre-cooled neutral atoms, to cryogenic temperatures of about 4 K. This lower temperature limit can be overcome using a laser-cooled buffer-gas localized at the center of the ion cloud.

In our hybrid atom-ion trap, the hydroxyl anions are stored in a 8-pole radio frequency wire trap and a dense cloud of ultracold rubidium is confined in a dark spontaneous-force optical trap (Dark-SPOT). The overlap of atoms and anions leads to elastic and inelastic collisions, cooling the external and internal degrees of freedom respectively. However, losses via associative detachment between OH⁻ and rubidium also occur, as predicted by ab-initio calculations. By varying the ratio of excited to ground state atoms, quantum state-dependent reactive collisions can be studied. Accurate measurements of these reactions can allow us to probe into the effective core potentials used in theoretical studies. In this contribution the latest results will be presented.

MO 2.2 Mon 10:45 S HS 1 Physik
State-to-state chemistry in a magnetic field — ●JOSCHKA WOLF, MARKUS DEISS, SHINSUKE HAZE, and JOHANNES HECKER DENSCHLAG — Institut für Quantenmaterie und Center for Integrated Quantum Science and Technology IQST, Universität Ulm, 89069 Ulm, Germany

State-to-state chemistry describes the determination of the quantum states of the final products given the quantum state of reactants. We have developed and demonstrated a method to probe diatomic molecular product states of reactive processes both qualitatively and quantitatively [1]. Using the given method, we have investigated the recombination of three neutral rubidium atoms in an ultracold atomic gas. We have extended the scheme of [1], to also resolve the magnetic quantum number of molecular product states. In this talk, we present

the measurements of product molecules for different reactant states as a function of the magnetic field. We find a propensity rule that the magnetic quantum number of the two reactants forming the molecule is conserved.

J. Wolf *et al.*, *Science* 358, 921 (2017)

MO 2.3 Mon 11:00 S HS 1 Physik
Sisyphus Optical Lattice Decelerator (SOLD) — ●RODRIGO GONZALEZ ESCUDERO, CHUN-CHIA CHEN, SHAYNE BENNETTS, BENJAMIN PASQUIOU, and FLORIAN SCHRECK — Van der Waals - Zeeman Institute, Institute of Physics, University of Amsterdam

In this talk, we present our implementation of a novel deceleration scheme that slows and cools atoms without using radiation pressure [1]. This scheme can enhance the efficiency of standard laser cooling techniques, requiring fewer photons to bring fast atoms to rest, making it a good decelerator candidate for exotic species [2] and molecules.

The SOLD works by having atoms selectively excited to an electronic state whose energy is spatially modulated by an optical lattice. Excited atoms decelerate solely by climbing the conservative potential landscape created by the lattice. The ensuing spontaneous decay brings atoms to the ground state, and completes one Sisyphus cooling cycle.

This deceleration method might prove useful for our attempt to create a steady-state strontium atom laser machine [3], breaching the gap from the currently achieved, and unprecedented steady-state phase-space density of near unity to the first steady-state Bose-Einstein condensate from which a continuous atom laser can be outcoupled.

[1] C.-C.Chen *et al.*, arXiv:1810.07157 (2018).

[2] S. Wu *et al.*, *Phys. Rev. Lett.* 106, 213001 (2011).

[3] S. Bennetts *et al.*, *Phys. Rev. Lett.* 119, 223202 (2017).

MO 2.4 Mon 11:15 S HS 1 Physik
Sympathetic cooling of molecular anions by a localized laser-cooled buffer gas — ●JONAS TAUCH¹, SABA ZIA HASSAN¹, ERIC ENDRES¹, MARKUS NÖTZOLD³, HENRY LÓPEZ¹, BASTIAN HÖLTKEMEIER¹, ROLAND WESTER³, and MATTHIAS WEIDEMÜLLER^{1,2} — ¹Physikalisches Institut Heidelberg, INF 226, 69120 Heidelberg — ²University of Science and Technology of China, Shanghai Branch, Shanghai, China — ³Institut für Ionenphysik und Angewandte Physik, Technikerstrasse 25/3, 6020 Innsbruck

Sympathetic cooling has become a powerful and universal method for preparing ultracold ions confined in radio frequency traps. This technique enables the study of cold molecular ions, as precision spectroscopy and chemistry at temperatures near to the absolute zero. In the past few years there has been a large debate about the limitations of this method, due to the mass ratio between the ions and the coolant. We developed a theoretical description which predicts that this limitations can be overcome by a localized buffer gas cloud and/or a higher order radio frequency trap. In this contribution I will present recent results of our hybrid atom-ion trap system, consisting of an 8-pole radio frequency wire trap and a dark spontaneous-force optical Rubidium trap. First signs of translational and rotational cooling of the trapped hydroxyl anions are observed. To probe the translational energy distributions of the anions, their time-of-flight is measured after extraction from the trap. The internal degrees of freedom are probed via near threshold photodetachment, revealing an increase of the population in lower rotational states. Thus cooling of the internal degrees of freedom.

MO 2.5 Mon 11:30 S HS 1 Physik

Using a Quartz Crystal Micro-Balance for the characterization of a Zeeman Slower — ●A. CHAVARRIA SIBAJA^{1,2}, A. GODINEZ SANDI^{1,2}, K. HERNANDEZ JIMENEZ^{1,2}, S. THIEL PIZARRO^{1,2}, M. GUEVARA BERTSH³, and O.A. HERRERA SANCHO^{1,2,4} — ¹Escuela de Física. University of Costa Rica — ²CICIMA. University of Costa Rica — ³Institut für Quantenoptik und Quanteninformatik. University of Innsbruck — ⁴CICANUM. University of Costa Rica

We present here the development of an experimental apparatus that consists of a Gd atoms source and 1 m-long multi-layer solenoidal Spin-Flip Zeeman Slower, and the propose of an alternative method to measure the atoms velocity, based on using of a Quartz Crystal micro-balance (QCM), which is normally used in thin film deposition process in solid-state physics. We observed that the measurement of the perturbations induced in the natural frequency of the QCM by the deposition mass process and the momentum exchange of the particles when they hit the crystal surface, allow to determine the change in the kinetic energy of Gd atoms. In this experiment, we focus a 447,2 nm laser into a counter-propagating beam of Gd atoms in order to drive the strongest dipole atomic transition from the ground 9D 0 state to the excited state 9D. Additionally we measure the variations of velocity of the atoms at the end of our Zeeman-Slower with a QCM, in order to characterize the effectiveness of our apparatus, as part of the future development of magneto-optical trap system. We obtain preliminary results of 39% of reduction of the velocity of the Gd atoms respect to their initial velocity using a current of 3 A.

MO 2.6 Mon 11:45 S HS 1 Physik

Locking of multiple Lasers to a Frequency Comb — ●BENJAMIN SPRENGER¹, DAG SCHMIDT¹, RONALD HOLZWARTH^{1,2}, BASTIAN HACKER², DOMINIK NIEMIETZ², and GERHARD REMPE² — ¹Menlo Systems GmbH, Am Klopferspitz 19a, 82152 Martinsried — ²Max-Planck Institut für Quantenoptik, Hans-Kopfermann-Straße 1, 85748 Garching bei München

Cold atom experiments usually require a whole set of lasers with different and precisely defined optical frequencies. A frequency comb offers the possibility to stabilize all lasers in the visible and near IR part of the spectrum (and even far beyond in the IR regime if needed) to the same reference, thereby providing the same stability and accuracy as well as mutual coherence to all lasers. We present a setup in which a frequency comb is used to stabilize more than 20 CW Lasers in 7 different laboratories. The comb light is distributed via optical fibers from the central comb laboratory to all other labs. Many applications, like quantum information experiments with single atoms and photons or molecular spectroscopy can be simplified with this setup and allows for reliable operations with improved accuracy.

MO 2.7 Mon 12:00 S HS 1 Physik

Improved Setup for Optoelectric Sisyphus Cooling of Formaldehyde Using a Detection Scheme Based on Laser Induced Fluorescence — ●MARTIN IBRÜGGER, MAXIMILIAN LÖW, ALEXANDER PREHN, MARTIN ZEPPENFELD, and GERHARD REMPE — Max-Planck-Institut für Quantenoptik, Hans-Kopfermannstr. 1, 85748 Garching

Ultracold molecules are ideal systems for the investigation of fundamental physics with applications ranging from quantum simulation over high-precision spectroscopy to ultracold chemistry. We showed in the past that optoelectrical Sisyphus cooling is one of the most promising techniques to provide the high number of molecules and the temperatures required for those applications [1]. We now implemented a new detection scheme for formaldehyde based on laser induced fluorescence (LIF), thereby increasing the signal by up to a factor of 30 compared to the previously used quadrupole mass spectrometer, and furthermore allowing state selective detection of the molecules.

Here, we present the current status of the experiment. In particular, we investigate trap dynamics of individual rotational M-sublevels which were previously hard to resolve. Results are very promising for the development of an improved cooling sequence which will pave the way for exciting applications such as high-precision spectroscopy and collisional studies of trapped formaldehyde.

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

MO 3: Ultrafast Processes in Solution

Time: Monday 10:30–12:30

Location: S HS 001 Biologie

Invited Talk MO 3.1 Mon 10:30 S HS 001 Biologie
Solvent-Specific Facets in the Ultrafast Photochemistry of Reactive Intermediates — JOHANNES KNORR¹, PANDIAN SOKKAR², SVENJA WORTMANN¹, PAOLO COSTA³, NIKLAS GESSNER¹, JULIEN ROWEN³, WOLFRAM SANDER³, ELSA SANCHEZ-GARCIA², and ●PATRICK NUERNBERGER¹ — ¹Physikalische Chemie II, Ruhr-Universität Bochum, 44780 Bochum — ²Computational Biochemistry, Universität Duisburg-Essen, 45141 Essen — ³Organische Chemie II, Ruhr-Universität Bochum, 44780 Bochum

Organic diazo compounds can release a nitrogen molecule upon photoexcitation, yielding very reactive species that will further pursue different reaction pathways on an ultrafast time scale. Among those pathways are rearrangement, intersystem crossing, intermolecular proton uptake, or complexation with a solvent molecule, giving rise to variable product distributions. The underlying processes strongly depend on the solvent environment and are accompanied by processes like solvation, vibrational cooling, and ion separation.

We will present an overview of recent femtosecond studies on diazo precursors excited in protic and aprotic solvents as well as in binary solvent mixtures. In combination with multiscale molecular dynamics simulations, we elucidate the reactivity of nascent intermediate carbenes and carbocations and the remarkable sensitivity to hydrogen-bonding among adjacent solvent molecules which take the role of key abettors rather than bystanders for the fate of the reactive intermedi-

ate. Variation of solvent mixing ratios thus provides a means to control the time scales and also the pursued pathways of the reaction.

MO 3.2 Mon 11:00 S HS 001 Biologie

Spectroscopic signatures of the dynamical hydration shell formation — ●HENNING KIRCHBERG¹, PETER NALBACH², and MICHAEL THORWART¹ — ¹Universität Hamburg, I. Institut für Theoretische Physik, Jungiusstr. 9, 20355 Hamburg — ²Westfälische Hochschule, Münsterstr. 265, 46397 Bocholt

The hydration shell, a specific formed water molecule network with hydrogen bonds near a solute, strongly influences the energetic and electronic properties of the solute and its (non-) solubility in a polar environment. The dynamical formation of a hydration shell is a process of central interest in many physical and chemical systems. We generalize the Onsager model of a static spherical cavity with a point dipole placed in a dielectric continuum solvent towards a dynamically varying Onsager sphere. In particular, we assume a dynamical growing layer of water around the central sphere. We calculate the response of the central molecular dipole to an external electric field in the presence of the dynamically growing layer. By this, we determine the energy cost for the solvation shell formation, which is responsible for the low solubility of hydrophobic agents in water. We find a frequency up-shift in the absorptive part of the response. Moreover, we are able to connect time-dependent spectroscopy signatures, i.e. the line width

of the absorption spectrum, to dynamical time scales of the hydration shell formation and to the characteristic fluctuations of the structured water within the hydration shell.

MO 3.3 Mon 11:15 S HS 001 Biologie
Broadband Ultrafast Transient Absorption Spectroscopy of Triplet Phenylpentadienylidene and Diphenylpropynylidene — ●LEA RESS, ENGELBERT REUSCH, HANS-CHRISTIAN SCHMITT, INGO FISCHER, and TOBIAS BRIXNER — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

The chemical and physical properties of unsaturated carbon-rich chain molecules like phenylpentadienylidene (PhC_5H) and diphenylpropynylidene (PhC_3Ph) are of significance in research areas such as astrochemistry and combustion processes, wherein biradical or rather carbenic structures and their electronic characteristics play an important role. Those molecules were previously generated by photolysis and characterized by matrix isolated EPR, IR and UV/Vis spectroscopy [1],[2]. Their precursors (5-diazopenta-1,3-dien-1-yl)benzene ($\text{PhC}_5\text{N}_2\text{H}$) and (3-diazoprop-1-yn-1,3-diyl)dibenzene ($\text{PhC}_3\text{N}_2\text{Ph}$) have not been characterized via ultrafast transient absorption spectroscopy in liquid phase at room temperature. In this contribution, we investigate the photolysis of the diazo group with ultrashort laser pulses by excitation at 260 nm to generate triplet PhC_5H and PhC_3Ph . We study the ultrafast photochemistry of these triplet species in dichloromethane and ethanol as aprotic and protic solvents, respectively, and further discuss reaction pathways and ultrafast dynamics up to three nanoseconds within these solvents.

- [1] S. N. Knezz et al., *J. Am. Chem. Soc.*, **138**, 12596-12604 (2016)
 [2] P. S. Thomas et al., *J. Org. Chem.*, **75**, 6372-6381 (2010)

MO 3.4 Mon 11:30 S HS 001 Biologie
Microsolvation vs. Acid Dissociation at 0.4 K: Sequence Matters — ●DEVENDRA MANI¹, RICARDO PÉREZ DE TUDELA², RAFAEL SCHWAN¹, NITISH PAL¹, SASKIA KÖRNING², HARALD FORBERT², BRITTA REDLICH³, LEX VAN DER MEER³, GERHARD SCHWAAB¹, DOMINIK MARX², and MARTINA HAVENITH¹ — ¹Lehrstuhl für Physikalische Chemie II, Ruhr-Universität Bochum, 44801 Bochum, Germany. — ²Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, 44780 Bochum, Germany. — ³FELIX laboratory, Institute for Molecules and Materials, Radboud University, 6525 ED Nijmegen, The Netherlands.

Acid dissociation in the aqueous medium is of fundamental importance. In order to understand the fundamental steps of this reaction, many experimental and theoretical studies have been carried out on small $\text{HCl-H}_2\text{O}$ clusters, in the past.[1-3]

We have studied the dissociation of HCl on stepwise addition of H_2O molecules, in helium droplets. Ultrabright pulsed-free electron lasers, at FELIX laboratory in Nijmegen, were used to measure the umbrella motion of the H_3O^+ moiety of the dissociated $\text{H}_3\text{O}^+(\text{H}_2\text{O})_3\text{Cl}^-$ cluster, in the frequency range of 1000-1700 cm^{-1} . Our experiments along with high-level ab initio MD simulations show that the dissociation of HCl is highly specific of the sequence in which molecular aggregation takes place. Details will be presented in the talk.

References: 1. H. Forbert, et al. *J. Am. Chem. Soc.*, 2011, **133**, 4062-4072. 2. A. Gutberlet et al., 2009, **324**, 1545-1548. 3. J. S. Mancini and J. M. Bowman, *Phys. Chem. Chem. Phys.*, 2015, **17**, 6222-6226.

MO 3.5 Mon 11:45 S HS 001 Biologie
Solvent-dependent time-resolved photoelectron spectroscopy study of relaxation dynamics in Quinoline Yellow — ●EVGENII

IKONNIKOV, JOHAN HUMMERT, and OLEG KORNILOV — Max-Born-Institute, Max-Born-Strasse 2A, Berlin, Germany

Relaxation dynamics of molecules often depends on their environment. In water, next to intramolecular relaxation processes, additional processes like solvent rearrangement and proton transfer upon photon absorption are possible. Recently we demonstrated pump-probe photoelectron spectroscopy in solution, which is a powerful tool for obtaining binding energies and lifetimes of molecular excited states of solvated molecules [1]. In our experiments we use a short XUV pulse as a probe pulse and 800/400 nm pulse as a pump pulse with pulse duration of 30 fs. In this contribution we will present measurements of relaxation dynamics of Quinoline Yellow (QY) in different solvents. In Ref. [1] we studied QY in water and observed three relaxation times: 250 ± 70 fs, 1.3 ± 0.4 ps and 90 ± 20 ps. We proposed that the two latter timescales may represent intramolecular proton transfer, while the fast timescale corresponds to solvent rearrangement. To clarify the nature of these processes we measure relaxation dynamics of QY in water with $\text{pH}=9$ and in heavy water to investigate the role of intermolecular proton transfer processes, which are expected to be slower for D_2O . [1] J. Hummert, G. Reitsma, N. Mayer, E. Ikonnikov, M. Eckstein and O. Kornilov, *J. Phys. Chem. Lett.*, 6649-6655, 9 (22), 2018.

MO 3.6 Mon 12:00 S HS 001 Biologie
(Time-resolved) Photoelectron circular dichroism in solution — JANINA LEBENDIG-KUHLE, PASCAL ENGL, HANS-HERMANN RITZE, and ●ANDREA LÜBCKE — Max Born Institute for Nonlinear Optics and Short Pulse Spectroscopy, Max-Born Strasse 2A, 12489 Berlin

Chiral systems play a very important role in nature, in particular in biology. Among the most widely spread chiral systems are DNA, amino acids, sugars, and peptides. We will investigate the role of chirality for the function of those molecules by the newly developed technique of (time-resolved) photoelectron circular dichroism in solution and provide new insights into the excited state dynamics of chiral systems. First results are presented for the model system fenchone, for tryptophan and a DNA nucleotide.

MO 3.7 Mon 12:15 S HS 001 Biologie
Experimental traces for ultrafast halogen-bond breaking in solution — ●BASTIAN GEISSLER¹, CHRISTIN PFLIEGER¹, CLAUDIO BEAKOVIC¹, ELRIC ENGELAGE², STEFAN HUBER², and PATRICK NUERNBERGER¹ — ¹Physikalische Chemie II, Ruhr-Universität Bochum, 44780 Bochum — ²Organische Chemie I, Ruhr-Universität Bochum, 44780 Bochum

Non-covalent halogen bonds between an iodine substituted organic compound and a Lewis base can play key roles in various chemical and biological processes. For instance, halogen bonds are already commonly used for crystal engineering. In the liquid phase, deciphering and exploiting the complex behavior of halogen bonds between solutes is an emerging area of research, still mostly focused on organic synthesis, catalysis, supramolecular self-assembly or molecular recognition processes.

In this study, we address the photophysical properties of compounds capable of halogen bonding by employing ultrafast time-resolved fluorescence upconversion and transient absorption techniques. Benzimidazole derivatives serve as halogen bond donors and pyridine derivatives as Lewis base acceptors. Absorption studies suggest the existence of iodine halogen bonds in acetonitrile solution, indicative of a modified charge distribution along the halogen bond which is only observable in the presence of the donor-acceptor pair. Upon excitation, signals assigned to the halogen bond rapidly disappear, suggesting that the halogen bond breaks reversibly within a few picoseconds.

MO 4: Electronic Spectroscopy

Time: Monday 10:30–12:30

Location: S HS 002 Biologie

Invited Talk MO 4.1 Mon 10:30 S HS 002 Biologie
Determination of Excited State Dipole Moments for Complex Systems - From Gas to the Condensed Phase — ●MICHAEL SCHMITT, MARIE-LUISE HEBESTREIT, MIRKO LINDIC, MATTHIAS ZAJONZ, and MICHAEL SCHNEIDER — Heinrich-Heine-Universität, Institut für Physikalische Chemie I, 40225 Düsseldorf, Germany

While in the gas phase, rotationally resolved electronic Stark spec-

troscopy is a versatile tool for the accurate determination of the permanent dipole moments in both states connected by the electronic transition, the situation in solution is less favorable. Although conceptually simple and broadly applied, solvatochromic shifts for the determination of excited state dipole moments are inaccurate and lead sometimes to completely false results.

A variant, using thermochromic shifts, leads to more reliable results, but still has some pitfalls. On the other hand many molecules

are thermally labile and cannot be brought into the gas phase without decomposition. In this contribution, we compare the values of excited state dipole moments from Stark spectroscopy with those from thermochromic shifts, and show some improvements to the method. The range of small (20 atoms) to large (more than 100 atoms) is covered, hereby.

MO 4.2 Mon 11:00 S HS 002 Biologie
Photoelectron circular dichroism observed on the nanosecond timescale — ●ALEXANDER KASTNER, TOM RING, ROXANA SAVULEA, HAN-GYEOL LEE, HENDRIKE BRAUN, ARNE SENFTLEBEN, and THOMAS BAUMERT — Universität Kassel, Institut für Physik und CINSaT, D-34132 Kassel, Germany

The asymmetry of photoelectron angular distributions from randomly oriented enantiomers of chiral molecules in the ionization with circularly polarized light arises in forward/backward direction with respect to the light propagation direction. This effect is known as photoelectron circular dichroism (PECD) and has been investigated by single-photon [1, 2] as well as resonance-enhanced multi-photon ionization using a femtosecond laser [3, 4]. Highly structured asymmetries in the range of $\pm 10\%$ on bicyclic Ketones were observed featuring pronounced dependence on photoelectron energy and electronic character of intermediate state for fenchone [5]. In addition, we were able to generalize the idea of a chiro-optical response to rotationally tailored fields [6].

Here we report on observation of PECD when using a Nd:YAG nanosecond laser. The possibility to use an ordinary nanosecond laser reduces the technical requirements to apply PECD in analytics.

- [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)
- [6] P. V. Demekhin et al., *PRL*, *accepted*, (2018)

MO 4.3 Mon 11:15 S HS 002 Biologie
Simulation of molecular photoelectron spectra within the Dyson orbital formalism — ●TOBIAS MÖHLE, SERGEY I. BOKAREV, and OLIVER KÜHN — Universität Rostock, Inst. f. Phys.

Photoelectron spectroscopy is an important tool for studying the electronic structure of molecular systems, but reliable predictions challenge theoretical models to date. In the weak-field limit, using a perturbative approach and neglecting inter-channel-interactions, the difficulties are two-fold: First, the bound electrons must be described accurately enough to obtain reasonable excitation energies in a wide range. Second, accurate intensities require a proper representation of the photoelectron wave function.

For the bound part we use time-dependent density-functional theory in combination with optimally tuned range-separated hybrid functionals. This leads to fairly good energetics in the valence region of water, benzene, Cu_4^- and S_8 . The level of approximation for the photoelectron spectrum influences the outcome strongly: The popular frozen-orbital approximation, where the transition energies correspond to the (Kohn-Sham) orbital energies, is outperformed by Dyson-orbital based simulations by far. Using the latter, the sudden approximation gives reasonable results in many cases. However, to account for the kinetic-energy-dependence of intensities, the photoelectron must be taken into account explicitly. While it is often described on a very approximate level, a route towards a more reliable description is presented, using a finite element scheme amended by infinite elements to ensure the correct asymptotic behaviour of the wave function.

MO 4.4 Mon 11:30 S HS 002 Biologie
Excited state dipole moment of 2-((4-methoxyphenyl)ethynyl)-3-(1-methyl-1H-indol-3-yl)quinoxaline via condensed phase thermochromic spectroscopy — ●MIRKO LINDIC, MATTHIAS ZAJONZ, TIM OBERKIRCH, and MICHAEL SCHMITT — Institute for Physical Chemistry I, Heinrich-Heine-University, Düsseldorf

The dipole moment of 2-((4-methoxyphenyl)ethynyl)-3-(1-methyl-1H-indol-3-yl)quinoxaline in the first excited singlet state was investigated using the method of thermochromic shifts of the fluorescence emission and absorption spectra.

Using the mentioned molecule as example some questions about the determination of excited state dipole moments in solution will be discussed: Which influence does the solvent cavity have dealing with large molecules? How is the dipole moment composed in a dye with multiple chromophores? How could quadrupole effects play a role in condensed

phase measurements?

The measurements results will also be compared with values from ab initio calculations to allow a critical view on the effects of solvent molecules in spectroscopic methods.

MO 4.5 Mon 11:45 S HS 002 Biologie
 Λ -doubling and Zeeman effect of $^2\Pi_{3/2}$ molecules in helium nanodroplets — ●WOJCIECH RZADKOWSKI and MIKHAIL LEMESHKO — Institute of Science and Technology Austria (IST Austria), Am Campus 1, 3400 Klosterneuburg, Austria

Fine-structure levels of $^2\Pi_{3/2}$ electronic state of diatomic molecules in the absence of external fields split into so-called Λ -doublets. In the presence of a magnetic field they split further, forming separate Zeeman levels. Both effects get strongly enhanced when the molecule is immersed into superfluid helium nanodroplets. This behavior lacks microscopic explanation, with only limited phenomenological models available.

We use the angular quasiparticle [1] to build a joint microscopic model explaining both anomalous Λ - and Zeeman splittings. Our approach does not use extensive numerical calculations. Instead, a physically intuitive picture of bath-induced couplings between fine-structure levels of the molecule is introduced. The theory can be verified against experimental data readily available for OH molecule [2].

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

[2] P. Raston, T. Liang, G. Douberly, Anomalous Λ doubling in the Infrared Spectrum of the Hydroxyl Radical in Helium Nanodroplets, *J. Phys. Chem. A* 117 (2013)

MO 4.6 Mon 12:00 S HS 002 Biologie
Optically-induced collapse of Mg foam in helium nanodroplets — ●LEV KAZAK¹, SEBASTIAN GÖDE², JOSEF TIGGESBÄUMKER¹, and KARL-HEINZ MEIWES-BROER¹ — ¹Institute of Physics, University of Rostock, Albert-Einstein-Str. 23-24, 18059 Rostock, Germany — ²European XFEL GmbH, Holzkoppel 4, 22869 Schenefeld, Germany

Magnesium embedded in helium droplets exist in form of metastable network of atoms surrounded by the layer of helium or so-called foam. At the conditions where only one Mg atom is presented in droplet, resonant two-photon ionization spectroscopy in the vicinity of $3^1P_1 \leftarrow 3^1S_0$ atomic transition reveals a narrow peak at 279 nm, blue-shifted relative to free atom. When the number of Mg atoms increases, a second peak at 282 nm arise and independent on further change of number of atoms. The presence of this feature, indicates that Mg atoms in He droplet have a interatomic distance of about 10 Å. In present work, the results on photoelectron spectroscopy of activated Mg foam are present. Instead of a single photoemission line, complex photoelectron spectra are obtained when several magnesium atom are present in the droplet, but almost no specific doping dependence is observed. New photoelectron peaks are attributed to highly excited states of Mg atoms. Analysis of electron yield with respect to pick-up statistics reveals the maximum number of Mg atoms which could be stabilized in foam. The behavior of photoelectron spectra indicates a foam collapse. The excess of energy during this process is transferred to single Mg atoms, leading to population of highly excited states.

MO 4.7 Mon 12:15 S HS 002 Biologie
Photo-dissociation of size and charge-state selected polyanionic tin clusters — ●MARKUS WOLFRAM, STEFFI BANDELOW, ALEXANDER JANKOWSKI, STEPHAN KÖNIG, GERRIT MARX, and LUTZ SCHWEIKHARD — Felix-Hausdorff-Straße 6, Institut für Physik, Greifswald, Deutschland

In contrast to various other metals that dissociate by monomer evaporation [1, 2], excited tin clusters offer a broad range of decay products, as observed after electron-cluster interactions [3]. To get further insight into their decay pathways, size and charge-state selected clusters $\text{Sn}_n^{1-/2-}$ were photo-excited at the ClusterTrap-setup [4] by 532-nm Nd:YAG laser pulses.

For small mono-anionic precursor clusters containing up to about $n = 50$ atoms, Sn_{n-7}^{1-} , Sn_{n-10}^{1-} or Sn_{n-15}^{1-} are observed as preferred fragments. For the bigger clusters (between ca. $n = 50$ to 70) there is a transition to monomer evaporation. In the case of di-anionic precursors, clusters Sn_{n-10}^{2-} come along with Sn_{n-10}^{1-} , probably due to fission as in the case of the group-14 neighbor-element lead [5]. Furthermore, doubly charged fragment clusters as Sn_{n-7}^{2-} appear - a special feature not observed previously for di-anionic clusters.

- [1] L. Schweikhard et al., Eur. Phys. J. D 36, 179 (2005)
 [2] A. Herlert et al., Int. J. Mass Spectrom. 249-250,215 (2006)
 [3] S. König et al., Eur. Phys. J. D 72, 153 (2018)

- [4] F. Martinez et al., Int. J. Mass Spectrom. 365-366, 266 (2014)
 [5] S. König et al., Phys. Rev. Lett. 120, 163001 (2018)

MO 5: Ultra-cold atoms and molecules II (joint session A/MO/Q)

Time: Monday 14:00–16:00

Location: S HS 1 Physik

MO 5.1 Mon 14:00 S HS 1 Physik

Spectroscopic studies on bosonic NaK — •KAI K. VOGES, PHILIPP GERSEMA, JANNIS SCHNARS, TORSTEN HARTMANN, TORBEN A. SCHULZE, ALESSANDRO ZENESINI, EBERHARD TIEMANN, and SILKE OSPELKAUS — Institut für Quantenoptik, Universität Hannover

With their large electric dipole moments and their rich internal level structures heteronuclear polar ground state molecules yield a rich test bed for a variety of dipolar phenomena.

In our experiment, we aim at the creation of ultracold bosonic ensembles of ground state polar $^{23}\text{Na}^{39}\text{K}$ molecules by means of Feshbach molecule association and subsequent two-photon transfer to rovibrational ground state polar molecules. This is a challenging task which requires detailed knowledge of the molecular level structure both at atomic threshold and at the bottom of the molecular potential.

In this talk we present our spectroscopic investigations on bosonic $^{23}\text{Na}^{39}\text{K}$ molecules. We perform microwave and radio frequency spectroscopy on bound Feshbach states identifying promising candidates for the initial association into shallow-bound states. Furthermore, we perform laser spectroscopy of the electronic excited $B^1\Pi(v=8)$ and $c^3\Sigma(v=30)$ coupled states. These data allow us to model the excited state manifold and determine the singlet-triplet mixing between these states. Moreover, we perform dark-resonance spectroscopy locating the two lowest lying rotational states in the molecular ground state potential. Finally, we will report on our progress to combine the different spectroscopic results for the creation of an ensemble of rovibrational ground state polar molecules.

MO 5.2 Mon 14:15 S HS 1 Physik

Pair superfluid phases in quasi one dimensional dipolar gases — •REBECCA KRAUS¹, KRZYSZTOF BIEDROŃ², JAKUB ZAKRZEWSKI^{2,3}, and GIOVANNA MORIGI¹ — ¹Theoretische Physik, Universität des Saarlandes, D-66123 Saarbrücken, Germany — ²Instytut Fizyki imienia Mariana Smoluchowskiego, Uniwersytet Jagielloński, Łojasiewicza 11, 30-048 Kraków, Poland — ³Mark Kac Complex Systems Research Center, Jagiellonian University, Łojasiewicza 11, 30-348 Kraków, Poland

We consider ultracold dipolar bosons in an optical lattice in a quasi-one dimensional geometry. We focus on the stability of pair superfluidity [1,2] as a function of the dipole interaction strength. We discuss the phases also for different power laws, such as van der Waals interaction between Rydberg dressed atoms.

[1] K. Biedroń et al., PRB 97, 245102 (2018) [2] T. Sowiński et al., PRL 108, 115301 (2012)

MO 5.3 Mon 14:30 S HS 1 Physik

Dipolar quantum droplets — •FABIAN BÖTTCHER, JAN-NIKLAS SCHMIDT, MATTHIAS WENZEL, JULIAN KLUGE, VIRAAAT SAI, JENS HERTKORN, TIM LANGEN, ARUP BHOWMICK, MINGYANG GUO, and TILMAN PFAU — 5. Physikalisches Institut and Center for Integrated Quantum Science and Technology IQST, Universität Stuttgart

The interplay of the short-range and isotropic contact interaction and the long-range and anisotropic dipolar interaction, allows for many interesting phenomena. In the case of the interactions competing with each other the mean-field contribution can get very small so that beyond mean-field effects start to play an important role and can actually stabilize an otherwise collapsing system. In our experiment with dysprosium atoms we observed a phase-transition between a gas and a liquid, characterized by the formation of self-bound droplets. These droplets show a saturation of the peak density with higher number of atoms like other liquids, even though they are 100 million times less dense than liquid helium droplets. The self-bound character of them opens up the new perspective of a truly isolated quantum system.

With our experiment we can study a single self-bound droplet and measure the critical atom number for the phase transition between liquid droplet and expanding gas for more than an order of magnitude.

For a single droplet we can also observe its anisotropic density distribution in-situ, as well as study the collective excitations. Furthermore the tendency of the system to form self-organized structures opens the possibility to reach a supersolid ground state.

MO 5.4 Mon 14:45 S HS 1 Physik

Anisotropic Superfluid Behavior of a Dipolar Bose-Einstein Condensate — •JAN-NIKLAS SCHMIDT, MATTHIAS WENZEL, FABIAN BÖTTCHER, TIM LANGEN, IGOR FERRIER-BARBUT, and TILMAN PFAU — 5. Physikalisches Institut and Center for Integrated Quantum Science and Technology IQST, Universität Stuttgart

Superfluidity still represents a hallmark of quantum physics. Its discovery in liquid helium was one of the first proofs for the influence of quantum effects at the macroscopic scale. The famous Landau criterion connects the maximal velocity for frictionless flow, mainly a transport property of such a superfluid, and its spectrum of elementary excitations. Later various transport measurements could show that also a Bose-Einstein condensate (BEC) features these properties, where the breakdown of superfluid flow can be probed by moving a microscopic impurity through the condensate. In case of a BEC of atoms with strong magnetic dipole-dipole interaction the breakdown of superfluid flow becomes directional, which directly can be seen as a probe of the anisotropic dipolar excitation spectrum.

During this talk we present transport measurements using a dipolar BEC of highly magnetic ^{162}Dy atoms, where we move an attractive laser beam through the condensate and observe an anisotropic superfluid flow. The critical velocity and the above starting heating rate is in excellent agreement with fully numerical simulations of the extended Gross-Pitaevskii equations that mimic our particular system.

MO 5.5 Mon 15:00 S HS 1 Physik

Self-bound ultracold Bose mixtures — •CLEMENS STAUDINGER¹, FERRAN MAZZANTI², and ROBERT E. ZILICH¹ — ¹Institute for Theoretical Physics, Johannes Kepler University Linz, Austria — ²Departament de Física i Enginyeria Nuclear, Universitat Politècnica de Catalunya, Spain

Recent experiments confirmed that fluctuations beyond the mean-field approximation can lead to self-bound liquid droplets of ultradilute binary Bose mixtures at very low temperatures. We study liquid Bose mixtures by using the variational hypernetted-chain Euler-Lagrange method, which accounts for correlations nonperturbatively. For the case of a uniform mixture, as it is found in the center of large droplets at saturation density, we study the conditions for stability against evaporation of one of the components (both chemical potentials need to be negative) and against liquid-gas phase separation, the spinodal instability. We discover that dilute Bose mixtures are stable only in a narrow range near an optimal ratio ρ_1/ρ_2 and in the vicinity of the total energy minimum. Despite the low density, deviations from a universal dependence on the s-wave scattering lengths are significant. We show how our results for uniform Bose mixtures can be extended to finite liquid droplets based on local density approximations.

MO 5.6 Mon 15:15 S HS 1 Physik

Bose polaron scenario in an ultracold Fermi-Bose mixture of ^6Li and ^{133}Cs — •ELEONORA LIPPI¹, BINH TRAN¹, MANUEL GERKEN¹, LAURITZ KLAUS¹, BING ZHU^{1,2}, MORITZ DRESCHER³, MANFRED SALMHOFER³, TILMAN ENSS³, and MATTHIAS WEIDEMÜLLER^{1,2} — ¹Physikalisches Institut, Ruprecht-Karls-Universität Heidelberg, Im Neuenheimer Feld 226, 69120 Heidelberg, Germany — ²Shanghai Branch, University of Science and Technology of China, Shanghai 201315, China — ³Institut für Theoretische Physik, Ruprecht-Karls-Universität Heidelberg, Philosophenweg 19, 69120, Heidelberg, Germany

An ultracold Fermi-Bose mixture of ^6Li and ^{133}Cs is an appealing playground to investigate the Bose polaron, a quasi-particle describing a single fermionic Li impurity immersed into a Bose-Einstein condensate

(BEC) of Cs and dressed by the phononic excitations of the condensate. The well-suited Feshbach resonances at high magnetic field provide a great degree of tunability of intra- and inter-species interactions, enabling us to explore both the repulsive and the attractive regime of the polaron. Due to the large Li-Cs mass ratio, signatures of 3-body Efimov physics in the energy spectrum of the polaron are expected. The observation of different polaron states from the Landau-Pekar polaron to the bubble polaron is also predicted for a Li-Cs mixture [1].

I will discuss how to combine a large BEC of Cs with Li impurities trapped into a microtrap, and our strategy for investigating Bose polaron's properties by means of radio-frequency spectroscopy.

[1] M. Drescher et al., arXiv:1810.11296 (2018)

MO 5.7 Mon 15:30 S HS 1 Physik

Exploring Fermi polarons across an orbital Feshbach resonance — •NELSON DARKWAH OPPONG^{1,2}, LUIS RIEGGER^{1,2}, OSCAR BETTERMANN^{1,2}, MORITZ HÖFER^{1,2}, JESPER LEVINSSEN³, MEERA M. PARISH³, IMMANUEL BLOCH^{1,2}, and SIMON FÖLLING^{1,2} — ¹Ludwig-Maximilians-Universität, München, Germany — ²Max-Planck-Institut für Quantenoptik, Garching, Germany — ³School of Physics and Astronomy, Monash University, Victoria, Australia

Ultracold atoms are a particularly clean system for probing polaronic states of interacting particles. Fermi polarons in particular have been studied with several realizations, all of which were using alkali atoms. Here, we report on the observation of attractive and repulsive Fermi

polarons across the orbital Feshbach resonance (OFR) in a two dimensional gas of ¹⁷³Yb. This novel type of Feshbach resonance allows tuning the s-wave scattering length of atoms in the ¹S₀ ground state and the metastable ³P₀ state. In our experiment, we prepare a spin-imbalanced Fermi gas for various interaction parameters $\ln(k_F a_{2D})$ in the vicinity of the OFR. We spectroscopically identify two distinct energy branches corresponding to attractive and repulsive Fermi polarons. In addition, we probe the quasiparticle properties, namely the quasiparticle residue and the lifetime of the repulsive polaron. We find good agreement between the experimental results and the predictions from our many-body theory.

MO 5.8 Mon 15:45 S HS 1 Physik

Quantum Zeno-based Detection and State Engineering of Ultracold Polar Molecules — •AMIT JAMADAGNI GANGAPURAM and HENDRIK WEIMER — Institut für Theoretische Physik, Leibniz Universität Hannover, Hannover, Germany.

We present a toolbox for the controlled manipulation of ultracold polar molecules, consisting of detection of molecules, atom-molecule entanglement and engineering dissipative dynamics. Our setup is based on fast chemical reactions between molecules and atoms leading to a quantum zeno based collisional blockade in the system. We discuss the optimization of the relevant parameters as well as the consequences of residual imperfections.

MO 6: Metal Complexes

Time: Monday 14:00–16:00

Location: S HS 001 Biologie

Invited Talk MO 6.1 Mon 14:00 S HS 001 Biologie

Investigation of structures and electronic states of transition metal containing complexes via transient FTIR spectroscopy — PATRICK DI MARTINO-FUMO¹, PIT BODEN¹, JASMIN BUSCH², SVEN OTTO³, KATJA HEINZE³, STEFAN BRÄSE², and •MARKUS GERHARDS¹ — ¹Physical Chemistry, TU Kaiserslautern, Germany — ²Organic Chemistry, KIT, Germany — ³Inorganic Chemistry and Analytical Chemistry, JGU Mainz, Germany

In order to analyze structures, electronic properties and lifetimes of transition metal complexes in their electronically excited states transient step-scan FTIR spectroscopy in the nanosecond and microsecond regime turns out to be a very efficient tool. We combine transient FTIR-spectroscopy with powerful tunable ns laser systems from the IR to the UV at different repetition rates which are used for specific electronic excitations. For investigation of temperature dependent effects samples can be cooled down to about 10 K. Furthermore different samples (solution, pellets, films) offer the possibility to analyze *e.g.* the influence of environment, aggregation state or electronic properties. The presented molecular systems include a series of bi- and tetranuclear Cu(I)-complexes relevant for the development of Iridium free OLEDs. Additionally Cr³⁺-containing complexes are mentioned which are efficient NIR emitters. Here newly developed double resonance techniques are presented, which are applied to specifically influence the relative population of two energetically similar electronically excited states.

MO 6.2 Mon 14:30 S HS 001 Biologie

Iron complexes as photosensitizers for hydrogen production — •BJÖRN ALTENBURGER¹, AYLA PÄPCKE¹, ALEKSEJ FRIEDRICH¹, STEFAN LOCHBRUNNER¹, PHILIPP DIERKS², PETER ZIMMER², and MATTHIAS BAUER² — ¹Institute of Physics, University of Rostock — ²Department of Chemistry, University of Paderborn

Iron is a promising candidate to replace rare transition metals in photosensitizer complexes used for light harvesting and photocatalytic applications. Even though its electronic properties are a severe obstacle to obtain a long living metal-to-ligand charge transfer (MLCT) state, the availability and environmental aspects make it worthwhile to investigate these complexes. In our research the focus is on Fe(II) complexes with N-heterocyclic carbene ligands which result in an enhanced ligand field. Our investigations using ultrafast transient absorption spectroscopy show that the lifetime of the MLCT state can be increased to several picoseconds utilizing these ligands [1]. Modifying them by adding electron withdrawing groups can prolong the lifetime even further. Recently, along this route developed iron complexes show even

fluorescence. Pump-probe measurements are combined with time resolved fluorescence spectroscopy to identify the relaxation pathways and to determine the lifetime of the involved states.

[1] P. Zimmer et al., Inorg. Chem. 2018, 57, 360-373

MO 6.3 Mon 14:45 S HS 001 Biologie

Optimally-tuned long-range corrected density functional for modeling excited states of spin-crossover iron complexes — •OLGA BOKAREVA, SERGEY BOKAREV, and OLIVER KÜHN — Institute of Physics, Rostock University, Albert Einstein Straße 23-24, 18059 Rostock

Transition metal complexes play an essential role as photosensitizers, photoemitters, and dyes. Although notable progress has been achieved with iridium(III) and ruthenium (III) complexes, the substitution of noble metals with earth-abundant and biocompatible elements is highly desirable from the viewpoint of overall costs and ecological impact. Iron compounds and especially spin-crossover complexes represent a convenient alternative but before going to real applications, profound mechanistic studies of excited state structure and dynamics, as well as the influence of chemical "tuning" on excited state order, should be performed. To this end, high-level theoretical studies are required to complement experiments.

In this work, we have applied optimally-tuned long-range corrected density functional theory for the modeling of ground- and excited state properties of a series of iron (III) spin-crossover complexes. The choice of the method is dictated by the objective to describe accurately long-range metal-to-ligand charge-transfer (MLCT) states which are of crucial importance for creating long-living excited states involved in further photocatalytic reactions. The character of singlet and triplet excited states is carefully analyzed and shown to be very sensitive to the applied computational scheme.

MO 6.4 Mon 15:00 S HS 001 Biologie

Singlet Oxygen Reactivity with Carbonate Solvents Used for Li-ion Battery Electrolytes — •MATTHIAS K. ROOS¹, ANNA T. S. FREIBERG², JOHANNES WANDT², HUBERT A. GASTEIGER², and REGINA DE VIVIE-RIEDLE¹ — ¹Department Chemie, Ludwig-Maximilians-Universität München, München — ²Lehrstuhl für Technische Elektrochemie, Technische Universität München, Garching

Increasing the energy density of modern Li-ion batteries is essential for their future widespread use in the automotive sector. To achieve this goal, new cathode active materials are required, for which mixed transition metal layered oxides are promising candidates. However, for high state of charge, the release of singlet oxygen was observed from these cathode materials, resulting in drastically reduced battery

lifetimes. In this joint experimental and theoretical work, we investigate the reactivity of the commonly used battery electrolytes ethylene carbonate (EC) and dimethyl carbonate (DMC) towards singlet oxygen [1]. Employing Rose Bengal to photochemically generate singlet oxygen in the bare electrolyte solutions, gaseous products are detected and quantified by on-line mass spectrometry. With quantum chemical and on-the-fly dynamical calculations a two-step reaction cascade is proposed, leading to the same products as found in the experiment. The uncommon reaction of an alkane with singlet oxygen in the first step constitutes the key element, activating the molecules for their further decay. The reaction mechanism is verified by colorimetric product detection in solution.

[1] *J. Phys. Chem. A* **122** (2018), 8828–8839.

MO 6.5 Mon 15:15 S HS 001 Biologie

Ultrafast processes in a luminescent mononuclear Cu(I) complex in liquid and solid phase — ●MERTEN GRUPE¹, FLORIAN BÄPPLER¹, MAXIMILIAN THEISS¹, FABIAN DIETRICH², STEFAN BRÄSE³, MARKUS GERHARDS², and ROLF DILLER¹ — ¹Dept. of Physics, TU Kaiserslautern, 67663 Kaiserslautern — ²Dept. of Chem., TU Kaiserslautern, 67663 Kaiserslautern — ³Dept. of Org. Chem., KIT, 76131 Karlsruhe

The primary photo induced processes in the OLED-usable mononuclear, heteroleptic Cu(I) complex ([DPEPhos]Cu[PyrTet]^[1]) were investigated in various solvents and solid state samples via femtosecond (fs) time resolved UV/Vis and fs time resolved mid-IR transient absorption spectroscopy (TA). Vibrational dynamics by mid-IR fs-TA are best described by a tri-exponential fit with $\tau_1 \approx 0.85$ ps, $\tau_2 \approx 5$ ps, $\tau_3 \approx 37$ ps. The UV/Vis data exhibit basically the same dynamics, however, dependent on the solvent a tri- or tetra-exponential fit is required. UV/Vis TA in solid phase leads to a tetra-exponential fit ($\tau_1 \approx 0.5$ ps, $\tau_2 \approx 2.6$ ps, $\tau_3 \approx 20$ ps, $\tau_4 \approx 200$ ps) as well, interestingly, with spectral dynamics significantly differing from that in solution. Based on our results we suggest that flattening distortion and/or a ligand twist (TD-DFT) occur on the time scale of τ_2 in solution and that, in contrast to literature on another mononuclear Cu(I) complex^[2], ISC (τ_3) is not necessarily associated with a spectral blue shift.

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

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

MO 6.6 Mon 15:30 S HS 001 Biologie

Time-resolved spectroscopy of the charge separation in Zn(III)-Au(III)-porphyrin dyads — ●AYLA PÄPCKE¹, SEBASTIAN PREISS², KATJA HEINZE², and STEFAN LOCHBRUNNER¹ — ¹Institut für Physik, Universität Rostock, Albert-Einstein-Str. 23, 18059 Rostock — ²Institut für Anorganische und Analytische Chemie, Johannes Gutenberg Universität Mainz, Duesbergweg 10-14, 55128 Mainz

To convert sunlight into chemical energy photoinduced energy transfer and electron transfer processes within the photosynthetic components are essential. Bioinspired systems contain porphyrins to mimic the role of chlorophyll in natural photosynthesis. Porphyrins are desired photosensitizers because of the easy functionalization, the strong absorption in the visible region, the often high fluorescence yield and the easy tunable redox properties [1].

Recently, gold(III) porphyrin cations have been used as electron acceptors in photosynthetic charge-separation [2]. Applying ultrafast transient absorption and time resolved photoluminescence spectroscopy we investigated the photoinduced electron transfer process of Zn(III)-Au(III)-porphyrin dyads and the dynamics of the formation of the Au(II) species.

[1] P. K. Poddutoori, *et al.*, *Phys. Chem. Chem. Phys.* **17**, 26346-26358 (2015)

[2] S. Preiß, *et al.*, *Nat. Chem.* **9**, 1249-1255 (2017)

MO 6.7 Mon 15:45 S HS 001 Biologie

Soft x-ray beam damage of a solid transition-metal complex — ●JAN LUDWIG¹, MARKUS KUBIN², ROLF MITZNER², CHRISTIAN WENIGER², ALEXANDER FÖHLISCH², JAN KERN³, VITTAL YACHANDRA³, JUNKO YANO³, and PHILIPPE WERNET² — ¹Max-Born-Institut für Nichtlineare Optik und Kurzzeitspektroskopie, Berlin, Germany — ²Helmholtz-Zentrum Berlin, Berlin, Germany — ³Lawrence Berkeley National Laboratory, Berkeley, USA

Soft x-rays are widely used for L-edge spectroscopy on transition-metal compounds, but also cause beam damage due to photoreduction. Here we determine the acceptable threshold of x-ray dose tolerable for L-edge absorption spectroscopy of a Mn(III) compound and discuss the underlying mechanisms. The results are important for acquiring damage-free L-edge spectra of transition-metal compounds in general.

MO 7: Experimental Techniques

Time: Monday 14:00–16:00

Location: S HS 002 Biologie

MO 7.1 Mon 14:00 S HS 002 Biologie

Enabling efficient coincident measurements of electrons and photons in the wavelength regime of 120 nm to 300 nm by a drastically increased solid angle for the photon detection — ●CHRISTIAN OZGA¹, PHILIPP SCHMIDT¹, ANDREAS NEHLS¹, GREGOR HARTMANN¹, XAVER HOLZAPFEL¹, CLEMENS RICHTER^{2,3}, JOHANNES VIEHMANN¹, PHILIP WENZEL¹, UWE HERGENHAHN^{2,4}, ARNO EHRESMANN¹, ANDRÉ KNIE¹, and ANDREAS HANS¹ — ¹Institute of Physics and Center for Interdisciplinary Nanostructure Science and Technology (CINSaT) University of Kassel Heinrich-Plett-Straße 40, 34132, Kassel, Germany — ²Leibniz Institute of Surface Modification Permoserstr. 15, 04318 Leipzig, Germany — ³Department of Physics, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany — ⁴Max Planck Institute for Plasma Physics Wendelsteinstr. 1, 17491 Greifswald, Germany

The coincident measurement of particles is a powerful tool for revealing and discriminating different de-excitation pathways. However, only few experiments detect photons due to the comparable small solid angle for their detection and therefore a low coincidence detection efficiency. We conceived a method for efficient coincident measurements of electrons and photons by a drastically increased solid angle for the photon detection. This set-up combined with a magnetic bottle time of flight spectrometer results in electron photon coincidence count rates appropriate for experiments at synchrotron radiation facilities, where beamtime is limited. Here we present measurements on atomic noble gases as prototypical samples to show the capabilities of the method.

MO 7.2 Mon 14:15 S HS 002 Biologie

Modeling the response of piezoelectric sensors used for detecting pulsed supersonic beams — ●PAUL SAFTIEN¹, KARSTEN LANGE², and WOLFGANG CHRISTEN¹ — ¹Humboldt-

Universität zu Berlin, Institut für Chemie, Brook-Taylor-Str. 2, 12489 Berlin, <http://clusterlab.de> — ²SLT Sensor- und Lasertechnik GmbH, Freiheitstr. 124-126, 15745 Wildau

In our studies [1] a piezoelectric polyvinylidene fluoride (PVDF) foil is used for the detection of pulsed supersonic beams [2]. Benefits of this method are a fast detector response, a ruggedized setup and the fact that no ionization is required. Experimental results performed in a wide range of source conditions (source pressures between 3 bar and 20 bar, source temperatures between -40 °C and 70 °C) show that the detector response is proportional to the momentum flux of scattered particles. A simultaneous measurement and evaluation of the background pressure in the vacuum chamber allows a calibration of the detector to the amount of atoms per pulse. The evaluation of the signal can be performed either numerically or analytically with a model function considering the electrical and mechanical properties of the piezoelectric detector.

[1] P. Saftien, K. Lange, W. Christen, to be submitted.

[2] *Z. Phys. Chem.* **228(4-5)**, 369 (2014), *J. Chem. Phys.* **139(15)**, 154202 (2013), *J. Chem. Phys.* **139(2)**, 024202 (2013).

MO 7.3 Mon 14:30 S HS 002 Biologie

Poly-Anion Production of Gas-Phase Clusters — ●STEFFI BANDELOW¹, FRANKLIN MARTINEZ², STEPHAN KÖNIG¹, GERRIT MARX¹, and LUTZ SCHWEIKHARD¹ — ¹Institute for Physics, University of Greifswald, 17487 Greifswald, Germany — ²Institute for Physics, University of Rostock, 18059 Rostock, Germany

While there is a long tradition in investigating cluster properties as function of the cluster size, varying the charge state opens another dimension. But especially for negative charge states, the production process often changes the cluster itself, e.g. when stabilising ligands

[1-2] or deprotonation [3] are used.

In an alternative approach, size selected aluminium gas-phase clusters are stored in a Penning trap simultaneously with electrons [4-5]. After an interaction time of 1s, the clusters are analysed with respect to the maximum number of excess electrons that have been attached. For the production of higher charge states, bigger clusters are required. Using clusters with up to 1950 atoms, gas-phase systems with up to 10 surplus electrons are produced and a quadratic dependence of the appearance size on the charge state is observed. This behaviour can be explained by considering the lifetimes of the meta-stable poly-anions.

- [1] M. K. Scheller et al., *J. Chem. Phys.* 100, 8943 (1994).
 [2] X.-B. Wang et al., *J. Chem. Phys.* 113, 10837 (2000).
 [3] S. Banerjee et al., *Int J Anal Chem* 2012, 282574 (2012).
 [4] F. Martinez et al., *Int. J. Mass Spectrom.* 266, 365 (2014).
 [5] F. Martinez et al., *J. Phys. Chem. C* 119, 10949 (2015).

MO 7.4 Mon 14:45 S HS 002 Biologie

Autofragmentation of rovibrationally excited anionic metal dimers on hours time scale — ●JÜRGEN GÖCK¹, ARNO BECKER¹, KLAUS BLAUM¹, CHRISTIAN BREITENFELDT^{1,2}, SEBASTIAN GEORGE^{1,2}, MANFRED GRIESER¹, FLORIAN GRUSSIE¹, ROBERT VON HAHN¹, PHILIPP HERWIG¹, JONAS KARTHEIN¹, CLAUDE KRANTZ¹, HOLGER KRECKEL¹, SUNIL KUMAR¹, JORRIT LION¹, SVENJA LOHMANN¹, CHRISTIAN MEYER¹, PREETI M. MISHRA¹, OLDŘICH NOVOTNÝ¹, AODH P. O'CONNOR¹, ROLAND REPNOW¹, KAIJA SPRUCK^{1,3}, STEFAN SCHIPPERS³, LUTZ SCHWEIKHARD², STEPHEN VOGEL¹, and ANDREAS WOLF¹ — ¹Max-Planck-Institut für Kernphysik (MPIK), Saupfercheckweg 1, 69117 Heidelberg, Germany — ²Institut für Physik, Ernst Moritz Arndt Universität Greifswald, 17487 Greifswald, Germany — ³I. Physikalisches Institut, Justus-Liebig-Universität Gießen, 35392 Gießen, Germany

The tunneling dissociation of ro-vibrationally excited Ag_2^- and Co_2^- was studied for up to 1000 s in the Cryogenic Storage Ring (CSR) [1] at the MPIK. The cryogenic environment below 6 K leads to a residual gas pressure of less than 10^{-14} mbar (room-temperature equivalent)-ideal conditions for background-free gas-phase spectroscopy. The anions were produced in a metal-ion sputter source, accelerated up to 60 keV and stored in the CSR. The neutral and charged fragments of the reaction $\text{X}_2^{*-} \rightarrow \text{X} + \text{X}^-$ were recorded by micro-channel-plate based detectors [2]. The data include coincidence signals from autodissociation of the anions as function of the storage time. The observed non-exponential nature of the decay will be discussed.

- [1] R. von Hahn et al., *Rev. Sci. Instrum.* 87, 063115 (2016)
 [2] K. Spruck et al., *Rev. Sci. Instrum.* 86, 023303 (2015)

MO 7.5 Mon 15:00 S HS 002 Biologie

Distinction of ortho-, meta- and para-benzene derivatives by means of chirped femtosecond laser ionization — ●VIOLA SCHÄFER and KARL-MICHAEL WEITZEL — Philipps-Universität Marburg, Fachbereich Chemie, Germany

The distinction of structural isomers, in particular ortho-, meta-, para-isomers of benzene derivatives poses a considerable challenge in situations, where chromatographic separation is not the method of choice. Distinction by means of electron impact mass spectrometry is in general not possible. Here, the combination of femtosecond laser ionization with time-of-flight mass spectrometry (fs-LIMS) constitutes an alternative, multi-dimensional technique with high analytical power. The variation of laser pulse parameters, e.g. the spectral phase, allows the distinction of structural isomers.[1] In the current work we present a systematic chirped fs-LIMS investigation of ortho-, meta- and para-isomers of fluorotoluene and fluorobenzyl bromide. The mass spectra for the isomers of the respective compound look similar for transform limited laser pulses. By variation of linear and quadratic chirp we are able to enhance small differences between the isomers for specific

fragmentation channels. We demonstrate, that we are able to distinguish the structural isomers of both compounds. In this context we will address the mechanism for the formation of common intermediates and the dynamics involved. The influence of the substituents and their positions at the benzene ring, as well as the relevance of specific fragments, e.g. tropylium and benzylium ions, will be discussed. [1] N. Reusch, V. Krein, N. Wollscheid, K.-M. Weitzel, *Z.f.Phys.Chem.*, 232, 689, (2018)

MO 7.6 Mon 15:15 S HS 002 Biologie

Setting up an experiment for electron-impact induced fluorescence spectroscopy of liquids — ●DANA BLOSS, ANDREAS HANS, PHILIPP SCHMIDT, CHRISTIAN OZGA, ARNO EHRESMANN, and ANDRÉ KNIE — Institut für Physik und CINSaT, Universität Kassel, Heinrich-Plett-Straße 40, 34132 Kassel

The investigation of liquids is a wide and interdisciplinary research field due to the fact that liquid water and aqueous solutions are the natural environment for many chemical and biological systems. However, the investigation of liquids with established experimental methods of atomic and molecular physics are challenging because of the typically required high vacuum conditions. With the development of the liquid microjet technique the investigation of volatile liquids in vacuum became possible. We already combined the liquid microjet with photon-impact induced fluorescence spectroscopy and observed a so far unknown broad emission between 170 - 340 nm which could be assigned to the liquid phase of the waterjet. For a better understanding of this emission feature we present an experiment for electron-impact induced fluorescence spectroscopy on liquid microjets. With this set-up secondary processes can be investigated by direct excitation of the liquid with electrons of kinetic energies ranging from 400 eV to 3 keV.

MO 7.7 Mon 15:30 S HS 002 Biologie

Phase-space imaging of nanoparticle beams — ●LENA WORBS^{1,2}, JANNIK LÜBKE^{1,3}, NILS ROTH^{1,2}, AMIT K. SAMANTA¹, DANIEL A. HORKE^{1,4}, and JOCHEN KÜPPER^{1,2,3,4} — ¹Center for Free-Electron Laser Science (CFEL), Deutsches Elektronen-Synchrotron DESY, Hamburg, Germany — ²Department of Physics, Universität Hamburg, Germany — ³Department of Chemistry, Universität Hamburg, Germany — ⁴The Hamburg Center for Ultrafast Imaging (CUI), Universität Hamburg, Germany

The generation and control of beams of internally cold biomolecules and nanoparticles is necessary for the production of reproducible samples, e.g., for single particle imaging experiments at x-ray free-electron lasers. The generation of those beams requires novel sample delivery methods and full characterization tools for nanometer sized particles in vacuum. Here, we present characterization methods that reconstruct the full 6D phase-space density of the beam for the optimization of nanoparticle beam sources.

MO 7.8 Mon 15:45 S HS 002 Biologie

Progress towards a molecular Zeeman slower — ●PAUL KAE-BERT, MARIA STEPANOVA, MAURICE PETZOLD, MIRCO SIERCKE, and SILKE OSPELKAUS — Institut für Quantenoptik, Leibniz Universität Hannover

The generation of large ultracold molecular ensembles is currently a challenge for researchers, due to the inefficient slowing methods available to them. In this talk I will summarize our efforts towards using our recently demonstrated Type-II Zeeman slowing technique to slow Calcium monofluoride (CaF) molecules. I will discuss the scheme and its implementation, as well as our approach for generating the laser light needed in the slowing process. Finally, I will discuss potential improvements to the design of our initial buffer gas beam source by comparing computational fluid dynamics simulations with flux and velocity profiles measured in the experiment.

MO 8: XUV and X-ray Excitation and Spectroscopy

Time: Monday 16:15–17:45

Location: S HS 001 Biologie

MO 8.1 Mon 16:15 S HS 001 Biologie

Time domain measurement of the ultrafast electronic decay of core excited HCl molecules by THz streaking — ●KATHARINA WENIG¹, MAREK WIELAND¹, SOPHIE WALTHER¹, ARNE BAUMANN¹, ANASTASIOS DIMITRIOU¹, MARK PRANDOLINI¹,

OLIVER SCHEPP¹, IVETTE BERMÚDEZ MACIAS¹, MALTE SUMFLETH¹, NIKOLA STOJANOVIC², STEFAN DÜSTERER², JULIANE RÖNTSCH-SCHULENBURG², MARKUS DRESCHER¹, and ULRIKE FRÜHLING¹ — ¹Institut für Experimentalphysik, Universität Hamburg, Deutschland — ²Deutsches Elektron-Synchrotron DESY, Hamburg, Deutschland

After excitation of 2p core electrons to the antibonding σ^* orbital the HCl molecules dissociate and the electronic excitation relaxes via an Auger decay. We have measured the ultrafast electronic decay of HCl molecules in the time domain.

In the experiment we addressed the 2p core electrons with 40 fs (FWHM) soft x-ray pulses from the free-electron laser in Hamburg (FLASH). Superimposing the pump pulse with intense THz light electrons emitted from the molecules are accelerated (streaked) by the THz electric field. Thereby, the resulting momentum change of the electron depends on the THz phase at the instant of ionization. We were able to measure the phase shift between the photo- and Auger electrons in the THz streak spectrograms and determine the Auger decay constant of the HCl molecule. In order to verify the resolution of our experiment the MNN Auger decay of Krypton atoms was investigated as well. The accuracy of the extracted value is on the order of two femtoseconds and therefore much below the duration of the exciting pump pulse.

MO 8.2 Mon 16:30 S HS 001 Biologie

Delayed relaxation of highly excited cationic states in naphthalene — GEERT REITSMA¹, JOHAN HUMMERT¹, JUDITH DURA¹, VINCENT LORIOU², MARC J. J. VRACKING¹, FRANCK LÉPINE¹, and OLEG KORNILOV¹ — ¹Max Born Institute, Berlin, Germany — ²Institut Lumière Matière, Université Lyon 1, CNRS, France

The efficiency of energy transfer in ultrafast electronic relaxation of molecules depends strongly on the complex interplay between electronic and nuclear motion. Modern tools of time-resolved spectroscopy allow investigation of these processes in "real" time. In this study we report two-color pump-probe experiments that probe the relaxation dynamics of highly excited cationic states of naphthalene, a prototypical polycyclic aromatic hydrocarbon molecule. The cations are produced using wavelength-selected, ultrashort extreme ultraviolet pulses and probed by subsequent ionization with a moderately-strong NIR pulses. Surprisingly, the observed relaxation lifetimes increase with the cationic excitation energy. We postulate that the observed effect is the result of a quantum mechanical population trapping that leads to delayed relaxation of molecules in the regions with high density of excited states. Comparison with previous results on relaxation dynamics of larger polyaromatic hydrocarbons suggests that this may be a general phenomenon in relaxation of PAH molecules.

MO 8.3 Mon 16:45 S HS 001 Biologie

Femtosecond dynamics in highly excited neutral CO₂: an experimental and theoretical study — THOMAS SCHNAPPINGER¹, MATTEO LUCCHINI², MARIO MURARI², GIACINTO D. LUCARELLI², LUCA POLETTI², FABIO FRASSETTO², MAURO NISOLI², and REGINA DE VIVIE-RIEDLE¹ — ¹Department of Chemistry, LMU Munich, Germany — ²Physics Department, Politecnico di Milan, Italy

The idea of this work is to combine an extreme UV (XUV) pulse and a few-femtosecond IR pulse in a pump-probe approach on carbon dioxide molecules. Here we want to present the first theoretical results obtained to interpret the experimental findings.

The dominant, almost constant, signal in the time dependent photoelectron spectrum arises from the direct ionization of the molecule just by the XUV pulse. A weaker oscillating signal with lower kinetic energy is also detected. The fastest observed period is around 28 fs.

Using high-level multi-reference methods (CASSCF and CASPT2) we are able to determine the electronic states of carbon dioxide in an energy range from 0 to 20 eV. Calculating the potential energy surfaces of various states it is possible to locate bound neutral states in the vicinity of the ionization threshold. The information of the static calculations in combination with the experimental results offers an interpretation of the weaker oscillating signal. The observed oscillation can be attributed to the vibrational motion of the nuclear wave packet in highly excited states around 1 eV below the ionization threshold.

MO 8.4 Mon 17:00 S HS 001 Biologie

XUV-photoion spectra from neutral gases measured with a radio frequency ion trap — SIMON REINWARDT¹, IVAN BAEV¹, KAROLIN MERTENS¹, FLORIAN TRINTER^{2,3}, and MICHAEL MARTINS¹ — ¹Institut für Experimentalphysik, Universität Hamburg, Hamburg, Germany — ²FS-PE, DESY, Hamburg, Germany — ³Molecular Physics, Fritz-Haber-Institut, Berlin, Germany

Photoion spectra of the neutral gases CO₂ and CH₄ were measured using a radio frequency ion trap at the soft X-ray beamline P04 of the synchrotron PETRA III at DESY in Hamburg. The used ion trap is part of the stationary Photon-Ion-Spectrometer (PIPE) [1]. In this experiment the neutral gas was photo ionized with monochromatized synchrotron light and the generated photoions were trapped in the radio frequency potential of the ion trap. In this way it was possible to measure a photoion NEXAFS spectrum at the carbon K-edge (290 eV) and for CO₂ also at the oxygen K-edge (535 eV).

Besides that we could show that the trapped ionized gas molecules are able to react with neutral gas to form larger molecular ions. At CO₂ we observed a small amount of CO₃⁺ and at CH₄ we found products with up to two carbon atoms. Depending on the resonant excitation, it is possible to change the generated ion as well as the electronic state of the ion so that the subsequent reaction is influenced. In addition similar measurements could be performed on ethene. Possible channels for these photochemical reactions will be discussed.

[1] S. Schippers et al., J. Phys. B: At. Mol. Opt. Phys 47, 115602, 2014.

MO 8.5 Mon 17:15 S HS 001 Biologie

Interrogating the Electronic Structure of Aqueous Diazines Using Non-Resonant and Resonant Soft X-ray Photoelectron Spectroscopy — MD SABBIR AHSAN^{1,2} and IAIN WILKINSON¹ — ¹Methods for Material Development, Helmholtz-Zentrum Berlin, Hahn Meitner platz 1, 14109 Berlin, Germany — ²Department of Physics, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany

Diazines play important roles in determining the photophysicochemical properties of bio-molecules such as DNA and RNA. We will present the electronic structure study of aqueous (aq.) diazines using liquid-microjet-based x-ray photoelectron spectroscopy (XPS). Valence band (HOMO) and core level C 1s and N 1s BE's are red shifted in aq. solution in comparison to the gas-phase. Preliminary surface- and bulk-sensitive studies on pyrimidine highlight an increase of N 1s BE's in the bulk compared to at the vacuum/liquid interface, whereas the C 1s spectra show the opposite behavior. Pyrimidine shows the lowest N 1s BE among the diazines in the surface-sensitive measurements. Moreover, resonant photoelectron spectroscopy (RPES) scans over the diazine N K-edges were recorded to study local and non-local relaxation processes in aq. solution. A number of core-valence resonances were identified and were found to be blue shifted compared to isolated gas phase molecules. Our study highlights solvent-induced electronic structure perturbations which are expected to provide information about the intra and intermolecular energy and proton transfer processes occurring in aq. diazine solutions following x-ray excitation.

MO 8.6 Mon 17:30 S HS 001 Biologie

Soft X-ray Absorption Spectroscopy of Aqueous Solutions Using a Table-Top Femtosecond Soft X-ray Source — CARLO KLEINE, MARIA EKIMOVA, GILDAS GOLDSZTEJN, SEBASTIAN RAABE, CHRISTIAN STRÜBER, JAN LUDWIG, SURESH YARLAGADDA, STEFAN EISEBITT, MARC VRACKING, THOMAS ELSAESSER, ERIK NIBBERING, and ARNAUD ROUZÉE — Max-Born-Institut

The advent of novel light sources like free electron lasers and high-harmonic generation (HHG) sources that offer the possibility to generate radiation in the soft X-ray wavelength range with femtosecond pulse durations has sparked widespread interest in the development of various forms of ultrafast, element-specific core-level spectroscopy. Here, we demonstrate the feasibility of soft X-ray absorption spectroscopy in the water window on organic molecules and inorganic salts in aqueous solution using a table-top laser-based approach. Using a high-order harmonic source that delivers femtosecond pulses of short wavelength radiation in the photon energy range from 220 eV to 450 eV, we report static soft X-ray absorption measurements in transmission mode on a series of solvated compounds using flatjet technology. We monitor the absorption of the molecular samples between the carbon (280 eV) and nitrogen (400 eV) K-edges and compare our results with previous measurements performed at the BESSYII facility. We discuss the roles of pulse stability and photon flux in the outcome of our experiments. Our experiment paves the way towards table-top femtosecond, solution phase soft X-ray absorption spectroscopy in the water window.

MO 9: Molecules in Intense Laser Fields

Time: Monday 16:15–17:45

Location: S HS 002 Biologie

MO 9.1 Mon 16:15 S HS 002 Biologie

Imaging experiments in the molecular frame — ●EVANGELOS T. KARAMATSKOS^{1,2,3}, SEBASTIAN RAABE⁴, TERRY MULLINS¹, ANDREA TRABATTONI¹, PHILIPP STAMMER⁴, GILDAS GOLDSZTEJN⁴, RASMUS R. JOHANSEN⁵, KAROL DLUGOLECKI¹, HENRIK STAPELFELDT⁵, MARC J.J. VRAKKING⁴, SEBASTIAN TRIPPEL^{1,3}, ARNAUD ROUZÉE⁴, and JOCHEN KÜPPER^{1,2,3} — ¹CFEL, DESY, Hamburg, Germany — ²Departments of Physics and Chemistry, Universität Hamburg, Germany — ³CUI, Universität Hamburg, Germany — ⁴Max-Born Institute, Berlin, Germany — ⁵Department of Chemistry, Aarhus University, Denmark

Imaging the ultrafast dynamics of molecules requires experimental methods, that offer atomic spatial and (sub-)femtosecond temporal resolution. The possibility to prepare cold, controlled molecular samples in the gas phase, combined with elaborate methods to fix the molecules in space, are important prerequisites to image molecular dynamics directly in the molecule-fixed frame. We present results on strong field-free alignment, achieved for the linear carbonyl sulfide (OCS) molecule and the complex, asymmetric top rotor indole. Furthermore, employing the laser-induced electron diffraction (LIED) method, the molecular structure of OCS could be retrieved with atomic resolution. Molecular-frame angularly-resolved photoelectron spectra show clear signatures of strong field photoelectron holography, which differ, depending on the orientation of the molecules with respect to the laser polarization of the ionizing field. A discussion of the observed interference patterns will be presented. References: Karamatskos et al., arXiv:1807.01034

MO 9.2 Mon 16:30 S HS 002 Biologie

A comparative study on ionization-induced dissociation of Methane, irradiated by 800 nm and 400 nm laser fields — LAZAROS VARVAREZOS¹, ALEXANDER ACHNER², ●RENÉ WAGNER², JOHN COSTELLO¹, MICHAEL MEYER², and PATRIK GRYSHTOL² — ¹School of Physical Sciences and NCPST, Dublin City University, Dublin 9, Ireland — ²Small Quantum Systems Group, European XFEL GmbH, 22869 Schenefeld, Germany

Irradiation of methane by intense laser fields leads to the production of several molecular ions CH_n^{m+} ($m = 1, 2$ with $n = 0 - 4$) and atomic fragments, such as H_n^{m+} ($m = 0, 1$ with $n = 1, 2$) as a result of dissociation [1]. Previous studies on methane ionization irradiated by pulses of nanosecond duration showed an absence of the parent fragment CH_4^+ . This was explained as a result of the dissociation into the CH_3^+ and a hydrogen atom. On the other hand, when the pulse duration was decreased down to a few femtoseconds all the fragment ions disappeared except for the CH_4^+ and CH_3^+ molecular ions indicating that methane did not have enough time to dissociate after the ionization step. All the aforementioned studies were confined to the fundamental wavelength of 800 nm. In the present work, we extend the study to include the second harmonic field at 400 nm.

[1] Mathur and Rajgara, Journal of Chemical Physics **124** (2006).

MO 9.3 Mon 16:45 S HS 002 Biologie

Static coherent states method: one and two electron laser-induced systems with classical nuclear dynamics — ●MOHAMMAD REZA EIDI¹, MOHSEN VAFAEE², and ALEXANDRA LANDSMAN^{1,3} — ¹Max Planck Institute for the Physics of Complex Systems, Dresden, Germany — ²Department of Chemistry, Tarbiat Modares University, Tehran, Iran — ³Max Planck Korea, Department of Physics, Postech, Pohang, Gyeongbuk 37673, Republic of Korea

In the presented work, the static coherent states method (SCS) is introduced to investigate quantum electron dynamics in a one or two-electron laser-induced system. The SCS method solves the time-dependent Schrödinger equation (TDSE) both in imaginary and real times on the base of a static grid of coherent states. Moreover, classical dynamics is considered for the nuclei by solving their Newtonian equation of motion. Implementing classical nuclear dynamics, the electronic state potential energy curves of H_2^+ in the absence and presence

of an ultra-short intense laser field is computed. We use this method to investigate charge migration in H_2^+ . In particular, we find that the charge migration time increases exponentially with internuclear distance. We also observe substantial charge localization for sufficiently long molecular bonds.

MO 9.4 Mon 17:00 S HS 002 Biologie

Probing electronic structure via molecular-frame photoelectron imaging — ●JOSS WIESE^{1,2}, SEBASTIAN TRIPPEL^{1,3}, and JOCHEN KÜPPER^{1,3,4} — ¹Center for Free-Electron Laser Science, Deutsches Elektronen-Synchrotron DESY, Hamburg — ²Department of Chemistry, Universität Hamburg — ³The Hamburg Center for Ultrafast Imaging, Universität Hamburg — ⁴Department of Physics, Universität Hamburg

Chemical function arises from the interplay among valence electrons. Thus, 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 molecular-frame photoelectron imaging of spatially confined ensembles of indole strong-field ionised by intense near-infrared laser pulses. Reconstructed static three-dimensional photoelectron distributions in molecular-frame momentum space (MF-ARPES) will be presented. The evaluation of the intensity differentials of these MF-ARPES allows for the mapping of the molecule's valence electronic structure and enables the investigation of strong-field ionisation phenomena in the intermediate regime between multi-photon and tunnel ionisation.

MO 9.5 Mon 17:15 S HS 002 Biologie

On the Role of singly-excited Rydberg states in Sequential H2 Multiphoton Ionization — ●PATRICK FROSS, DENHI MARTINEZ, NICOLAS CAMUS, THOMAS PFEIFER, and ROBERT MOSHAMMER — Max-Planck-Institut für Kernphysik, Heidelberg, Germany

Nowadays Sequential Multiphoton Ionization of H₂ is mainly understood in terms of a stepwise mechanism. First the ground state molecule is ionized by removing one electron. Then eventually dissociation takes place and finally there is a chance of removing the second and last electron. We present COLTRIMS results that show that this mechanism is not correct for 35fs laser pulses with a central wavelength of 400nm ($I=1 \cdot 10^{14}$ W/cm²). Our observations demonstrate that singly-excited Rydberg states play a major role in the dynamics of photoionization. In addition the underlying ionization pathway is explained.

MO 9.6 Mon 17:30 S HS 002 Biologie

An alternative dissociation pathway of N_2^{2+} — LAZAROS VARVAREZOS¹, ●ALEXANDER ACHNER², RENÉ WAGNER², JOHN COSTELLO¹, MICHAEL MEYER², and PATRIK GRYSHTOL² — ¹School of Physical Sciences and NCPST, Dublin City University, Dublin 9, Ireland — ²Small Quantum Systems Group, European XFEL GmbH, 22869 Schenefeld, Germany

Since the advent of lasers as spectroscopic tools, N_2 has served as a benchmark system to shed light on the phenomena induced by intense laser fields. In our study, we focus on the dissociation mechanism of the molecular dication N_2^{2+} . Our interest in the dication was stimulated by a study that revealed the presence of two different $N^+ + N^+$ states, energetically separated by about 4eV for the first time [1]. Our findings suggest the presence of two ion pairs, separated by approximately 2eV originating from fast and slow decay channels. Most likely, the fast pair of ions stems from the $^1\Sigma_g^+$ state after the removal of two $3\sigma_g$ electrons, while the slow ion pair results from the $^3\Pi_u$ state of the molecular ion after the removal of one $3\sigma_g$ electron and one $1\pi_u$ electron. Furthermore, we reach to the very important conclusion that the slow channel is the precursor for the N_2^{2+} ions, due to the existence of a strong intensity dependence, which is not present in the case of the faster ions.

[1] Lai et al., Physical Review A **84**, 043413 (2011).

MO 10: Posters 1: Cold Molecules, High Resolution Spectroscopy, and Theory

Time: Tuesday 16:30–18:30

Location: S Foyer LLM

MO 10.1 Tue 16:30 S Foyer LLM

A narrow-line rotational-state-dependent dipole trap for ultracold polar molecules — ●XING-YAN CHEN¹, ROMAN BAUSE¹, MING LI², SCOTT EUSTICE¹, MARCEL DUDA¹, FRAUKE SEESSELBERG¹, SVETLANA KOTOCHIGOVA², IMMANUEL BLOCH^{1,3}, and XIN-YU LUO¹ — ¹Max-PlanckInstitut für Quantenoptik, Hans-Kopfermann-Str. 1, 85748 Garching, Germany — ²Department of Physics, Temple University, Philadelphia, PA 19122-6082, USA — ³Ludwig-Maximilians-Universität, Schellingstraße 4, 80799 München, Germany

Ultracold polar molecules in rotational states with opposite parities offer strong dipole-dipole interaction, thus can be used to encode pseudo-spin and simulate spin models with long-range interactions. We demonstrate a rotational-state-dependent dipole trap for ultracold $^{23}\text{Na}^{40}\text{K}$ molecules by utilizing a narrow-line rotational transition manifold $|X^1\Sigma^+, v=0, J=0, 1\rangle \rightarrow |b^3\Pi, v=0, J=0, 1, 2\rangle$. By selecting an appropriate laser detuning, we are able to make a "magic" trap where the polarizabilities of $|J=0, 1\rangle$ states are the same, an "anti-magic" trap where the polarizabilities are exactly opposite, or a tune-out trap where the polarizability of one of the rotational states vanishes. Further more, thanks to the narrow natural linewidth of the excited $|b^3\Pi_0+, v=0\rangle$ state, the photon-scattering of the tune-out trap is negligible. A long-lived universal spin-dependent dipole potential will facilitate novel studies of spin models and many-body localization with ultracold polar molecules.

MO 10.2 Tue 16:30 S Foyer LLM

Spectroscopic characterization of the $a^3\Pi \leftarrow X^1\Sigma^+$ and $A^1\Pi \leftarrow a^3\Pi$ transitions of aluminium monofluoride — STEFAN TRUPPE¹, SILVIO MARX¹, SEBASTIAN KRAY¹, ●MAXIMILIAN DOPPELBAUER¹, SIMON HOFSSÄSS¹, HANNS CHRISTIAN SCHEWE¹, BORIS SARTAKOV², and GERARD MEIJER¹ — ¹Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin, Germany — ²General Physics Institute, Russian Academy of Sciences, Vavilostreet 38, 119991 Moscow, Russia

Aluminium monofluoride is proposed as an excellent candidate molecule for laser cooling and trapping. For this, detailed knowledge of the low-lying rotational levels in the involved $X^1\Sigma^+$, $A^1\Pi$ and $a^3\Pi$ states is necessary.

The energy levels in the $X^1\Sigma^+$, $v=0$ state and within each Ω -manifold in the $a^3\Pi$, $v=0$ state are determined with a relative accuracy of a few kHz, using laser - radio-frequency multiple resonance ionization detection schemes in a jet-cooled, pulsed molecular beam.

The strength of the spin-forbidden $A^1\Pi$, $v=0 \leftarrow a^3\Pi$, $v=0$ transition is measured to be between six and seven orders of magnitude lower than that of the $A^1\Pi$, $v=0 \leftarrow X^1\Sigma^+$, $v=0$ transition.

MO 10.3 Tue 16:30 S Foyer LLM

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

Because of their rich internal structure and long-range dipole-dipole interactions, cold polar molecules have great potential for a wide variety of different applications. In our experiment, we are able to cool formaldehyde (H_2CO) down to sub-millikelvin temperatures by applying optoelectrical Sisyphus cooling [1]. In the past, the molecules were detected in a robust and reliable way using a quadrupole mass spectrometer. However, the low detection efficiency of $\sim 10^{-4}$ led to long measurement times thereby severely limiting the experiment.

Here, we present a new detection setup based on laser-induced fluorescence (LIF) of formaldehyde. A quantum yield of up to 30% for radiative decay from the excited state and light collection optics covering a solid angle of $\sim 70\%$ lead to an increase in detection efficiency of up to a factor of 30. A high signal to noise ratio was achieved by reducing background light by many orders of magnitude. Additionally, we can now detect molecules state selectively, including discrimination of different rotational M-sublevels. This makes LIF detection a powerful tool which will enable us to substantially improve our understanding of our experiment and promises exciting future prospects.

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

MO 10.4 Tue 16:30 S Foyer LLM

Building a Zeeman slower for CaF molecules — ●MARIIA STEPANOVA, PAUL KAEBERT, MAURICE PETZOLD, MIRCO SIERCKE, and SILKE OSPELKAUS — Institut für Quantenoptik, Leibniz Universität Hannover

We will report on our progress towards realizing a large flux source of ultracold Calcium monofluoride (CaF) molecules using molecular Zeeman slowing. We will give details of our test experiment, demonstrating the feasibility of the technique using ^{39}K . As a first step to implementing our method in molecules we have constructed and characterized a cryogenic buffer gas source, capable of producing molecules with a mean velocity of 150m/s. By comparing our results to simulations using computational fluid dynamics we will discuss several ways to improve on our initial buffer gas cell design, and present data on the molecular flux using our improved cell geometry. Because sufficient laser power is essential for efficient Zeeman slowing of molecules, we will also present data on generating a high power beam of 606nm Laser light through sum frequency generation. By combining all these systems, we hope to finally give current experiments the source they need to produce a quantum degenerate gas of ultracold molecules.

MO 10.5 Tue 16:30 S Foyer LLM

Sympathetic cooling and quantum state dependant reactions of molecular anions by a localized laser-cooled buffer gas — ●ERIC ENDRES¹, JONAS TAUCH¹, SABA HASSAN¹, MARKUS NÖTZOLD², BASTIAN HÖLTKEMEIER¹, HENRY LOPEZ¹, ROLAND WESTER², and MATTHIAS WEIDEMÜLLER¹ — ¹Physikalisches Institut Heidelberg, INF 226, 69120 Heidelberg — ²Institut für Ionenphysik und Angewandte Physik, Technikerstrasse 25/3, 6020 Innsbruck

Buffer gas cooling is a versatile technique to cool ions confined in a cryogenic radiofrequency ion traps[1]. However, it is limited to temperature of the coolant, typically being about 4K. By using a laser cold atom cloud, this limitation can be overcome. Furthermore, by localizing the atom cloud and/or a higher order radio frequency trap, theoretical description predicts cooling beyond the critical atom to ion mass ratio [2, 3].

In this contribution I will present recent results of our hybrid atom-ion trap system [4], consisting of an 8-pole radio frequency wire trap confining OH^- and a dark spontaneous-force optical Rubidium trap [5]. By embedding ultra cold atoms in an ion cloud, three kind of collisions can occur. First, elastic collisions leading to cooling of the external degrees of freedom from the hydroxy anion, second inelastic collisions leading to cooling of the internal degrees of freedom. Finally, reactive collisions, namely associative detachment reactions, leading to a loss of the trapped anion.

First sings of sympathetic cooling will be shown, as well as, reactive collisions depending on the quantum state of the Rubidium atoms.

MO 10.6 Tue 16:30 S Foyer LLM

Spectroscopic characterization of aluminium monofluoride with relevance to laser cooling and trapping — STEFAN TRUPPE¹, SILVIO MARX¹, SEBASTIAN KRAY¹, MAXIMILIAN DOPPELBAUER¹, ●SIMON HOFSSÄSS¹, CHRISTIAN SCHEWE¹, BORIS SARTAKOV², and GERARD MEIJER¹ — ¹Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin, Germany — ²General Physics Institute, Russian Academy of Sciences, Vavilovstreet 38, 119991 Moscow, Russia

The aluminium monofluoride molecule (AlF) is an excellent candidate for laser cooling and trapping. Prior to this, it is necessary to measure the detailed energy level structure in the $X^1\Sigma^+$ electronic ground state, in the $A^1\Pi$ state and in the metastable $a^3\Pi$ state as well as the strength of the transitions between these states. We here report the results of spectroscopic measurements between the $X^1\Sigma^+$ and the $A^1\Pi$ state.

MO 10.7 Tue 16:30 S Foyer LLM

Observation of cold dipolar collisions and electrostatic trapping of centrifuge decelerated molecules — ●MANUEL KOLLER, THOMAS GANTNER, FLORIAN JUNG, ISABEL RABEY, MARTIN ZEPPENFELD, and GERHARD REMPE — Max-Planck-Institute of Quantum Optics, Garching, Germany

Dense samples of cold polar molecules provide fascinating research pos-

sibilities in physics and chemistry. By combining cryogenic buffer gas cooling and centrifuge deceleration we recently demonstrated a record high flux exceeding 10^{10}s^{-1} and densities up to 10^9cm^{-3} of cold polar molecules at kinetic energies corresponding to less than 1K [1]. This allows the observation of cold molecule-molecule collisions for CH_3F and ND_3 . The low absolute velocity enables the straightforward loading of molecules into an electrostatic trap [2], making much more detailed collision studies possible due to longer interaction times. Beyond the observation of inelastic collisions, the creation of highly nonthermal energy distributions by sharply cutting away hotter molecules with a radio frequency knife should allow the investigation of rethermalization via elastic collisions.

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

[2] B. Englert et al., Physical Review Letters 2011, 106, 263003

MO 10.8 Tue 16:30 S Foyer LLM

Modifications and simulations for a Velocity Map Imaging device aiming for methane activation by transition metal cations — •LISA-MEDARDA RETTER, JENNIFER MEYER, TIM MICHAELSEN, BJÖRN BASTIAN, FRANZISKA KRAMMER, and ROLAND WESTER — Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck, 6020 Innsbruck, Austria

Our aim is to image the dynamics of transition metal cations with small hydrocarbons, namely the system of tantalum ions with methane [1,2]. In order to study elementary reaction dynamics and energy distributions into different products we operate our experiment under single collision conditions. This is achieved by crossing a neutral molecular beam with an ion beam produced by a laser vaporization source. Detection is managed via velocity map imaging, which allows for the measurement of differential cross sections [3]. We have recently enhanced the experimental setup with alterations in the form of a conductance limiter as well as a supplementary detector for the ion beam. Simulations in SIMION for these modifications as well as currently planned ones are shown for the system of tantalum cations reacting with methane. [1] H. Schwarz. Angew. Chem. Int. Ed. Engl., 1991, 7, 30 [2] L.G. Parke, C.S. Hinton, P. B. Armentrout. J. Phys. Chem. C 2007, 111, 17773-17787. [3] R. Wester, PCCP, 2014, 16, 396

MO 10.9 Tue 16:30 S Foyer LLM

Monte Carlo simulation of a cryogenic buffer gas cell — •THOMAS GANTNER, MANUEL KOLLER, MARTIN ZEPPEFELD, and GERHARD REMPE — Max-Planck-Institut für Quantenoptik, 85748 Garching, Deutschland

Cryogenic buffer gas cells have been a workhorse for the cooling of molecules for more than 20 years. The straightforward sympathetic cooling principle makes it applicable for a huge variety of different species. Notwithstanding this success, detailed simulations of buffer gas cells are rare, and limited to high buffer gas density regimes, when the mean free path of a molecule is small compared to all dimensions of the cell. Here, we present a new numerical approach based on a molecule trajectory analysis. The implementation following the Monte Carlo method can reproduce the flux of molecules emerging from the buffer gas cell for varying buffer gas densities. Furthermore, it can reproduce the velocity distribution of the resulting molecule beam. This includes the so-called boosting effect, when buffer gas atoms accelerate the molecules after leaving the cell. The simulations provide various insights which could substantially improve buffer-gas cell design.

MO 10.10 Tue 16:30 S Foyer LLM

Cavity design for spatial resolved detection of cold molecules — •JANNIS SCHNARS^{1,2}, ALESSANDRO ZENESINI², SILKE OSPELKAUS², and KLEMENS HAMMERER¹ — ¹Leibniz Universität Hannover, Institut für Theoretische Physik, 30167 Hannover — ²Leibniz Universität Hannover, Institut für Quantenoptik, 30167 Hannover

Ultracold polar molecules offer promising research perspectives in particular due to their strong dipole-dipole interactions. Recently there has been tremendous progress in the creation and manipulation of ultracold polar molecules. The highest phase space densities have been achieved by associating molecules from ultracold ensembles of atoms in a controlled way. However, when it comes to imaging, established techniques for the destructive and non-destructive imaging of atoms fail for molecules due to the complex structure of molecules with vibrational and rotational degrees of freedom. Typically, imaging of ultracold molecules is therefore achieved by reversing the creation process of ultracold molecules and subsequently image atoms on an atomic cycling transition. However, it would be desirable to directly image molecules, ideally non-destructively and with high spatial resolution.

Here we present a scheme to detect molecules inside a 2D-optical lattice. The detection relies on an induced phase shift due to off-resonant light matter interaction. The phase shift is enhanced by a small-waist multimode cavity. We identify possible resonator geometries which balance the requirements for a small beam waist and the need to support several frequency degenerate transverse mode facilitating spatial resolution of several lattice sites.

MO 10.11 Tue 16:30 S Foyer LLM

IR spectroscopy of glycine-water in helium nanodroplets — •NITISH PAL¹, DEVENDRA MANI¹, RAFFAEL SCHWAN¹, GERHARD SCHWAAB¹, BRITTA REDLICH², LEX VAN DER MEER² und MARTINA HAVENITH¹ — ¹Physikalische Chemie II, Ruhr-Universität Bochum, Germany — ²Institute for Molecules and Materials (IMM), Radboud University Nijmegen, Nijmegen, Netherlands

We have studied the microsolvation of glycine with water molecules using helium droplet isolation infrared spectroscopy. Glycine exists in neutral form in gaseous state and in zwitterionic form in aqueous solutions. We address the question: "what is the minimum number of water molecules required to convert a neutral glycine molecule to its zwitterionic form?" The stepwise addition of water molecules to one glycine molecule was achieved using helium droplets isolation technique. The superfluid helium droplets allow a barrier free diffusion of the dopant molecules and enable the formation of large molecular clusters. The infrared spectra were recorded in the range of $1000\text{-}1850\text{ cm}^{-1}$, using the free electron lasers (FELs) at FELIX laboratory in Nijmegen.

MO 10.12 Tue 16:30 S Foyer LLM

Analysis of the coupled $(2)^2\Sigma^+$ and $(1)^2\Pi$ of LiSr — •ERIK SCHWANKE, JULIA GERSCHMANN, HORST KNÖCKEL, SILKE OSPELKAUS, and EBERHARD TIEMANN — QUEST und Inst. f. Quantenoptik, Leibniz Universität Hannover

We present a description of several vibrational states of the $(1)^2\Pi$ state of LiSr. Although the $(1)^2\Pi$ state is not directly visible in our recorded infrared spectra due to a weak transition dipole moment to the $X(1)^2\Sigma^+$ state, we could use observed perturbations in the $(2)^2\Sigma^+$ state to model the coupling between the spectroscopically observed $(2)^2\Sigma^+$ state and the $(1)^2\Pi$ state.

The coupling model leads to a description of the rotational ladders of the coupled $v' = 0$ and $v' = 1$ states of $(2)^2\Sigma^+$ and several vibrational states of both $(1)^2\Pi_{1/2}$ and $(1)^2\Pi_{3/2}$, thus giving local rotational and vibrational constants, as well as the spin-orbit coupling constant for the $(1)^2\Pi$ states. Relative overlap integrals for the involved vibrational states of $(1)^2\Pi$ and $(2)^2\Sigma$ are derived. Furthermore, the perturbation reveals the correct assignment of the F_1 and F_2 levels in the $(2)^2\Sigma^+ - (1)^2\Sigma^+$ system.

We will report on the status of the investigations.

MO 10.13 Tue 16:30 S Foyer LLM

Investigation of quadrupole moment effects on the determination of excited state dipole moments in solution — •MATTHIAS ZAJONZ, TIM OBERKIRCH, MIRKO LINDIC, and MICHAEL SCHMITT — Institute for Physical Chemistry I, Heinrich-Heine-University Düsseldorf

The molecule under investigation, 2,5-cyclohexadiene-1,4-dione (p-benzoquinone), is highly symmetric and by looking at its structure it is obvious that it has a quadrupole moment instead of a dipole moment.

To improve thermochromic methods for determination of excited state dipole moments in solution the effects of quadrupole moments have to be investigated.

For the molecule under investigation we measured thermochromic shifts, in order to assess the influence of quadrupole moments on the dipole moment determination in electronically excited states.

MO 10.14 Tue 16:30 S Foyer LLM

The influence of vibrational excitation on the reaction of F^- with CH_3I — •TIM MICHAELSEN, BJÖRN BASTIAN, JENNIFER MEYER, and ROLAND WESTER — Institut f. Ionenphysik und Angewandte Physik, Universität Innsbruck

We study ion molecule reaction dynamics in a crossed beam setup using velocity map imaging [1]. One focus of our research are reactions of halide anions with methylhalides, which represent an interesting model system to study bimolecular nucleophilic substitution reactions ($\text{S}_\text{N}2$). In recent years we have extended our investigations of such systems to study microsolvation effects as well as the influence of vibrational

excitation on branching ratios and reaction dynamics [2].

Here we report on recent results investigating the influence of C-H stretch excitation on the reaction of F^- with CH_3I at various collision energies. The CH_3I is excited by a broadband OPO/OPA laser prior to collision and the excited fraction is probed using a photodissociation and state selective REMPI scheme. The experimental results are compared with recently published quasiclassical trajectory calculations for the same system [3].

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

[2] M. Stei, et al., Sci. Adv. 4, 7, eaas9544 (2018)

[3] B. Olsasz and G. Czako, J. Phys. Chem. A, 122, 41, 8143-8151 (2018)

MO 10.15 Tue 16:30 S Foyer LLM

Intramolecular scattering: Simulation of coupled electron-nuclear motion upon photoionization — FRIEDRICH GEORG FRÖBEL, ●ALEXANDER SCHUBERT, and STEFANIE GRÄFE — Friedrich-Schiller-Universität Jena, Jena, Germany.

We theoretically investigate intramolecular scattering and energy redistribution during photoionization of molecular systems in intense few-cycle XUV laser fields. The molecular model system is described by the extended Shin-Metiu model consisting of two position-fixed nuclei with one movable nucleus in between and two electrons in a single dimension. Dynamics simulations are performed by integrating the time-dependent Schrödinger equation numerically using grid-based methods. Spectral signatures in the photoelectron spectra are shown to contain sensitive information about different ionization pathways revealing the ionization-induced electron and nuclear dynamics and subsequent non-adiabatic effects.

MO 10.16 Tue 16:30 S Foyer LLM

A modified approach for simulating nonadiabatic dynamics via the generalized quantum master equation — ELLEN MULVIHILL¹, ●ALEXANDER SCHUBERT^{1,2,3}, XIANG SUN^{1,4}, BARRY D. DUNIETZ², and EITAN GEVA¹ — ¹University of Michigan, Ann Arbor, MI, United States — ²Kent State University, Kent, OH, United States — ³Friedrich-Schiller Universität Jena, Jena, Germany — ⁴New York University Shanghai, Shanghai, China

A modified approach for simulating nonadiabatic dynamics based on the Nakajima-Zwanzig generalized quantum master equation (GQME) is presented. Unlike the most common GQME-based approaches, the modified approach (M-GQME) does not require casting the overall Hamiltonian in a (not uniquely defined) system-bath form, which is neither natural nor convenient in the case of the molecular Hamiltonian that governs the nonadiabatic dynamics. Within the M-GQME framework, the effect of the degrees of freedom of the environment on the time evolution of the reduced density operator is fully captured by a memory kernel superoperator. In the presented numerical implementation, the memory kernel is calculated employing the Ehrenfest mean-field method. The modified approach is demonstrated on a benchmark spin-boson model and shown to lead to significantly more accurate results than a direct application of the Ehrenfest method while being computationally more robust than other GQME-based approaches.

MO 10.17 Tue 16:30 S Foyer LLM

A classical ride through a conical intersection — ●THOMAS SCHAUPP and VOLKER ENGEL — Institut für Physikalische und Theoretische Chemie, Emil-Fischer-Str. 42, 97074 Würzburg, Germany

Regarding the correlated electron-nuclear motion in a model system, we investigate the dynamics in the vicinity of a conical intersection (CoIn) between two excited state potential surfaces. It is documented that an ensemble of classical trajectories which move in the complete electronic-nuclear phase space tracks the quantum wave-packet motion through the CoIn which is accompanied by a strong non-adiabatic population transfer. On the contrary, for an adiabatic circular motion around the position of the CoIn, the quantum mechanical and classical densities deviate substantially. In the latter case, the Born-Oppenheimer classical nuclear motion on a single potential surface is able to track the quantum dynamics.

MO 10.18 Tue 16:30 S Foyer LLM

First principles calculation of molecular partial autoion-

ization rates — ●GILBERT GRELL, OLIVER KÜHN, and SERGEY BOKAREV — Universität Rostock, Rostock, Deutschland

Autoionization processes such as Auger and interatomic coulombic decay play a key role in the radiation matter interaction on atomic and molecular scales. For instance, the lifetime of a core excited state is primarily defined by its autoionization rate. Further, autoionization cascades after initial ionization or excitation determine the resulting ion and electron yields. First principles calculations of partial autoionization rates are demanding due to the necessary description of continuum states. Standard quantum chemistry (QC) codes usually employ Gaussian basis sets, which describe bound states and orbitals very well. Continuum orbitals, however, are poorly described by these basis sets, prohibiting a simple extension of standard QC methods to include continuum states. We present a protocol that aims at estimating autoionization energies and partial rates, based on standard QC calculations for the bound states that are supplemented with continuum orbitals. A single center model is used to reduce the continuum orbital problem to the solution of a radial Schrödinger equation in the potential of the remaining ion. In this framework we assess the impact of different approximations to the radial potential on the continuum orbitals and resulting partial autoionization rates. Finally, the general applicability of the single center model for the calculation of molecular autoionization rates is analyzed.

MO 10.19 Tue 16:30 S Foyer LLM

Optimized Sampling of Mixed-State Observables — ●MAREC W. HEGER, CHRISTIANE P. KOCH, and DANIEL M. REICH — Theoretische Physik, Universität Kassel, Heinrich Plett-Straße 40, 34132 Kassel, Germany

Quantum dynamical simulations of statistical ensembles pose a significant computational challenge due to the fact that mixed states need to be represented by a density matrix instead of a wave function. If the underlying dynamics are fully unitary, for example in coherent control at finite temperatures, one approach to approximate time-dependent observables in this context is to sample the density matrix by solving the Schrödinger equation for a set of wave functions with randomized phases.

We present an in-depth analysis of the average performance for the random-phase wave functions and compare them to deterministic sampling of the energetically lowest-lying eigenstates. In particular, the performance crossing point between these two approaches allows an estimation of the more efficient sampling scheme for an average observable. Moreover, we prove that minimization of the worst-case error among arbitrary observables is uniquely attained by eigenstate-based sampling. Finally, we point out how the structure of low-rank observables can be exploited to further improve eigenstate-based sampling schemes.

MO 10.20 Tue 16:30 S Foyer LLM

Comparison of two different ways to calculate expectation values — ●KLAUS RENZIEHAUSEN and INGO BARTH — Max Planck Institute of Microstructure Physics, Weinberg 2, D-06120 Halle (Saale), Germany

We analyze two different ways to calculate quantum mechanical expectation values for several observables. The first ansatz is just the direct calculation of the quantum mechanical expectation value, the second ansatz is to calculate this expectation value using the Ehrenfest theorem. We have performed those calculations for the temporal mass change, the momentum, the force, the torque, and the angular velocity of a particle in three dimensions. As a result, we found for each of these observables an integral equation. On one side of this equation an integrand depending on the mass density appears, while we find on the other side an integrand depending on the mass current density. So, we can calculate these expectation values either using the mass density or the mass current density (as an exception the analysis for the expectation value of the azimuth angular velocity is more complicated). This has application possibilities for molecular systems where electronic current densities cannot be calculated within the Born-Oppenheimer approximation. The papers [I. Barth et al., Chem. Phys. Lett. **481**, 118-123 (2009)] and [T. Schaupp, J. Albert, V. Engel, Eur. Phys. J. B **91**, 97 (2018)] can be interpreted as examples for such applications.

MO 11: Photochemistry

Time: Wednesday 10:30–12:30

Location: S HS 001 Biologie

Invited Talk MO 11.1 Wed 10:30 S HS 001 Biologie
Properties of multiazobenzene systems - old dogs and new tricks — ●CHAVDAR SLAVOV¹, CHONG YANG², LUCA SCHWEIGHAUSER³, ANDREAS H. HEINDL³, TIM STAUCH², HERMANN A. WEGNER³, ANDREAS DREUW², and JOSEF WACHTVEITL¹ — ¹IPTC, Goethe University, Frankfurt, Germany — ²IWR, University of Heidelberg, Heidelberg, Germany — ³IOC, Justus Liebig University, Giessen, Germany

Azobenzenes (AB) are extensively used in the development of photo-switchable nanostructures. While the photochromism of single ABs is studied in detail, the behavior of connected ABs is not well understood. We combine ultrafast spectroscopy and quantum chemical calculations to explore the properties of different multi-AB constructs [1-4]. The arrangement and the interactions of the individual photoswitch units alter the photochemistry of these systems and give rise to a variety of new molecular properties - intramolecular excitonic coupling, extended π -delocalization, molecular strain, etc. Based on our results, we conceptualize a single-molecule triple photoswitch, with selectively addressable units [4]. Such a system can be used in functional nano-materials as a hub integrating the response to different signals. In the light of the wide spread construction and utilization of photoresponsive compounds, our studies bring new and important insights.

- [1] C. Slavov, et al., PCCP, 18, 14795 (2016)
- [2] C. Slavov, et al., ChemPhysChem, 18, 2137 (2017)
- [3] C. Slavov, et al., JPC Lett., 9, 4776 (2018)
- [4] C. Yang, et al., Chem. Sci, DOI: 10.1021/acs.jpcclett.8b02159

MO 11.2 Wed 11:00 S HS 001 Biologie
Azobenzene isomerization probed by photon spectroscopy — ●MARIO NIEBUHR¹, ANDRÁS BÓDI², PATRICK HEMBERGER², FABIANO LEVER¹, DENNIS MAYER¹, JAN METJE¹, MATTHEW ROBINSON¹, DOMENIK SCHLEIER³, INGO FISCHER³, and MARKUS GÜHR¹ — ¹Institute for Physics and Astronomy, Uni Potsdam, Germany — ²VUV Spectroscopy Group, PSI, Switzerland — ³Institute for Physical and Theoretical Chemistry, Uni Würzburg, Germany

Azobenzene's characteristic trans-cis isomerization, a fully reversible and esp. UV/Vis excitable process, is a good model system for photo-addressable molecular switches. While the molecule itself and its derivatives are well on their way from purely scientific interest towards real-world applications, the underlying isomerization mechanics are still being researched. Prominent examples are the intermediate molecular geometries while switching between the two isomeric states or in our case the Kasha rule violation observable in the trans and cis isomerization yield after excitation to the S_1 resp. S_2 state.

We will present first findings from combining ultra-fast UV pump-probe ion time-of-flight spectroscopy with quasi-cw, synchrotron based VUV fragmentation studies on isolated azobenzene molecules in the gas phase. Former yields time dependent information on form and distance between electronic levels while the later allows us to deduce the initial excited state of the parent molecule from the observed fragments. Thus, we get a better image of the ionic states involved in the itof experiment to characterize and understand the relaxation pathway during the isomerization process.

MO 11.3 Wed 11:15 S HS 001 Biologie
Time-dependent mass spectra studies of gas-phase trans-stilbene oxide as probed by ultrafast UV pump-probe laser techniques — ●MATTHEW S. ROBINSON, MARIO NIEBUHR, and MARKUS GÜHR — Institut für Physik und Astronomie, Universität Potsdam, Potsdam, Germany.

The photo-chemical ring-opening mechanisms of oxirane-based molecules are heavily dependent on the substituent groups attached to the molecule. Photo-excited unsubstituted and alkyl-substituted oxiranes favor cleavage of the C-O bond, whilst cyano- and aryl-substituted oxiranes cleave at the C-C bond and open in disrotary fashion, in agreement with Woodward-Hoffman rules. [1]

However, in direct contrast to these rules, theory predicts that there is no favored route between the conrotary and disrotary opening paths of photo-excited aryl-substituted oxiranes, despite the conrotary motion rarely being observed. [2] In order to better understand these systems we have performed time-resolved UV pump-probe mass spectra studies on gas-phase trans-stilbene oxide (trans-2,3-diphenyloxirane).

Here we present the results from these experiments, detailing information on the lifetimes of the observed fragments, as well as what this informs us about the photo-excited state of stilbene oxide.

1. Woodward, R. B. & Hoffmann, R., Angew. Chemie 81, 797-870 (1969).
2. Friedrichs, J. & Frank, I. Chem. - A Eur. J. 15, 10825-10829 (2009).

MO 11.4 Wed 11:30 S HS 001 Biologie
Tuning Excited-State Proton Transfer of a Super-Photoacid — ●NIKLAS SUELZNER¹, BASTIAN GEISSLER¹, ALEXANDER GRANDJEAN², GREGOR JUNG², and PATRICK NUERNBERGER¹ — ¹Physikalische Chemie II, Ruhr-Universität Bochum, 44780 Bochum — ²Biophysikalische Chemie, Universität des Saarlandes, 66123 Saarbrücken

Special molecules, referred to as photoacids, exhibit an acidity increase upon irradiation. Triggered by photoexcitation, such molecules perform an excited-state proton transfer (ESPT) if suitable proton acceptors are present. Moreover, super-photoacids, i.e. with a negative pK_a value in the excited-state, are even strong enough for ESPT in non-aqueous solution. In previous studies, we observed ESPT from the neutral, super-photoacidic HPTS-derivative hydroxypyrenetris(hexafluoropropanylsulfonate) to acetone. However, the influence of water on ESPT in this aprotic environment remained unresolved.

The present study investigates the ESPT kinetics of this photoacid in binary acetone-water mixtures by time-resolved fluorescence spectroscopy on the picosecond timescale. Owing to the fluorescence of both the protonated and deprotonated species, information on ESPT is hereby directly accessible through the fluorescence dynamics. First, we reveal the severe effect of water in the mixtures constituting in an acceleration of ESPT with increasing concentration. Afterward, we demonstrate that the water-driven acceleration can be antagonized by adding an excess of strong acid. Based on this, we infer that strong acids can be used to effectively deactivate water towards ESPT.

MO 11.5 Wed 11:45 S HS 001 Biologie
Steering proton transfer pathways of the bifunctional photoacid 7-hydroxyquinoline — ●MARIUS-ANDREI CODESCU and ERIK T. J. NIBBERING — Max-Born-Institut für Nichtlineare Optik und Kurzzeitspektroskopie, Max-Born-Str. 2A, 12489 Berlin

Acid-base neutralization reactions in protic solvents typically occur through proton exchange pathways consisting of a solvent bridge connecting acid and base. Bifunctional photoacids have both proton donating and accepting sites, enabling real-time probing of proton exchange through a well-defined number of solvent molecules. For 7-hydroxyquinoline (7HQ), compelling evidence pointed to initial proton abstraction by the quinoline N site from the methanol solvent, followed by methoxide transport to the OH-site, making it a proton hole transport [Hoffmann et al., J. Phys. Chem. A 120, 9378 (2016)]. This strongly contrasts to the generally accepted picture of an excess proton transport pathway initiated at the OH-site. Here we show that by adding formate anion to 7HQ in methanol, the dominant proton transport pathway of 7HQ changes from a transmission of proton holes to that of excess protons. We follow the reaction dynamics by probing IR-active marker modes of 7HQ and of formic acid with femtosecond time resolution, and determine the local parameters that open up the excess proton transport route. Our findings may provide insight into proton transport pathways of transmembrane proton channel proteins.

MO 11.6 Wed 12:00 S HS 001 Biologie
Ultrafast dissociation of vinyl bromide after passage through a conical intersection: an experimental and theoretical study — FLORIAN ROTT¹, MAURIZIO REDUZZI^{2,3}, ●THOMAS SCHNAPPINGER¹, STEPHEN R. LEONE^{2,4,5}, and REGINA DE VIVIER-RIEDLE¹ — ¹Department of Chemistry, LMU Munich, Germany — ²Department of Chemistry, University of California, Berkeley, USA — ³ICFO - The Institute of Photonics Sciences, The Barcelona Institute of Science and Technology, Spain — ⁴Chemical Sciences Division, Lawrence Berkeley National Laboratory, USA — ⁵Department of Physics, University of California, Berkeley, USA

The ultrafast dissociation of vinyl bromide after strong-field excitation is characterized experimentally and theoretically. After a multiphoton

excitation of the $\pi\pi^*$ transition, the relaxation process is illuminated via Attosecond Transient Absorption Spectroscopy (ATAS) using the bromine M-edge. This method allows to monitor the evolution of the nuclear wave packet during the dissociation of bromine within 100 fs.

Using non-adiabatic molecular dynamics in combination with high-level multi-reference methods we are able to simulate the corresponding time-dependent transient absorption spectrum of vinyl bromide. The simulated spectrum shows a good agreement with the experimental ATAS trace in the relevant energy range.

This joint experimental and theoretical work provides insight into the nuclear dynamics of dissociating vinyl bromide.

MO 11.7 Wed 12:15 S HS 001 Biologie

Controlling the dynamics of the photodissociation of diphenylmethyl bromide — •FRANZISKA SCHÜPPEL, MATTHIAS K. ROOS, and REGINA DE VIVIE-RIEDLE — Department Chemie, Ludwig-Maximilians-Universität München

Carboradicals and -cations are key intermediates for many chemical reactions and can be generated by UV-laser excitation from certain precursor molecules. Recently, we investigated the photodissociation of diphenylmethyl bromide using quantum dynamics simulations. [1] The dynamics is characterized by two consecutive conical intersections (CoIns) with the first one leading to the favored homolytic dissociation channel.

The control of the ratio of homolytic and heterolytic bond cleavage is of major interest for chemical applications. By using a second few-cycle IR laser pulse it is possible to create a superposition of a wave packet at a CoIn and by that control the population transfer through that CoIn. [2] We want to apply such a laser pulse to diphenylmethyl bromide to explore to which extend the population transfer of the wave packet through the first CoIn can be disabled. By that we want to regulate the branching between carbocation and carboradical formation.

[1] F. Schüppel *et al.*, *PCCP* **20** (2018), 22753-22761.

[2] P. von den Hoff *et al.*, *PCCP* **14** (2012), 14460-14485.

MO 12: High Resolution Spectroscopy and Precision Experiments

Time: Wednesday 10:30–12:30

Location: S HS 002 Biologie

MO 12.1 Wed 10:30 S HS 002 Biologie

Rotationally Resolved Electronic Stark Spectroscopy of 2,3-Benzofurane — •MARIE-LUISE HEBESTREIT, MICHAEL SCHNEIDER, HILDA LARTIAN, and MICHAEL SCHMITT — Institute for Physical Chemistry I, Heinrich-Heine-University, Düsseldorf

The electronic origin of 2,3-benzofurane has been investigated using high resolution laser induced fluorescence spectroscopy (HRLIF) to analyze its electronic nature. The obtained molecular parameters from evolutionary algorithms were compared to the results of *ab initio* calculations. To investigate the permanent dipole moments in the ground and first excited state a homogeneous field was applied, which lifts the M degeneracy due to the Stark effect. Finally, the orientation of the transition dipole moment for the monomer is discussed and compared to that of indole in particular.

MO 12.2 Wed 10:45 S HS 002 Biologie

Rotationally Resolved Electronic Stark Spectroscopy of 4-cyanoindole — •MARIE-LUISE HEBESTREIT, MICHAEL SCHNEIDER, HILDA LARTIAN, and MICHAEL SCHMITT — Institute for Physical Chemistry I, Heinrich-Heine-University, Düsseldorf

High resolution electronic Stark spectroscopy is a valuable tool to determine the electronic nature of substituted indoles. Both, 3- and 5-cyanoindole were already investigated via high resolution spectroscopy and the electronic nature of their first excited states were identified as L_b -state for 3-cyanoindole and L_a -state for 5-cyanoindole, respectively. Now, 4-cyanoindole and its N-deuterated analogon were studied, evaluated via evolutionary algorithms and compared to the results of *ab initio* calculations. The rotational constants, permanent dipole moments in the ground and first excited state, the orientation of the transition dipole moment and the fluorescence lifetime were determined and used to identify the lowest excited singlet state as a L_a -state. Finally a view on the diverging fluorescence lifetimes of different cyanoindoles is given in this talk.

MO 12.3 Wed 11:00 S HS 002 Biologie

Predicting *para-ortho* conversion in ammonia — •GUANG YANG^{1,4}, VINICIUS SILVA DE OLIVEIRA^{2,4}, CHRISTOPH HEYL², ANDREY YACHMENEV^{1,3}, INGMAR HARTL², and JOCHEN KÜPPER^{1,3,4} — ¹Center for Free-Electron Laser Science, DESY, Notkestrasse 85, Hamburg — ²DESY, Notkestrasse 85, Hamburg — ³The Hamburg Center for Ultrafast Imaging, Luruper Chaussee 149, Hamburg — ⁴Department of Physics, University of Hamburg, Luruper Chaussee 149, Hamburg

We present a combined theoretical and experimental study of the hyperfine-resolved spectrum of ammonia and its deuterated isotopologues. The calculations have been performed using the 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 with up to 8000 cm^{-1} above the zero-point-energy level.

For the spectroscopic observation of the *para-ortho* interconversion we use mid-infrared frequency comb spectroscopy in both ammonia vapour and a cold molecular beam. Furthermore, its modulation by external electric field is discussed. Our theoretical model, i.e., the underlying potential energy surface will be refined using the experimentally observed transitions.

MO 12.4 Wed 11:15 S HS 002 Biologie

Triphenylmethane and all-*meta tert*-butyl triphenylmethane dimers: Observation of an unusual C-H...H-C distance in the gas phase via stimulated Raman spectroscopy — •DOMINIQUE MAUÉ¹, DOMINIC BERNHARD¹, PATRICK H. STREBERT¹, SÖREN RÖSEL², PETER R. SCHREINER², and MARKUS GERHARDS¹ — ¹Physical Chemistry, TU Kaiserslautern, Germany — ²Organic Chemistry, JLU Gießen, Germany

Recently a dimerization of triphenylmethane (TPM) and all-*meta tert*-butyl triphenylmethane ($T^t\text{BuPM}$) has been observed in crystals which leads in the case of $T^t\text{BuPM}$ to an unusually short C-H...H-C contact. In order to find out if this is a pure intrinsic behavior of the molecules, we report here on molecular beam investigations on isolated dimers by applying stimulated Raman spectroscopy with our new Raman setup. In combination with DFT calculations (including dispersion corrections) the formation of the head-to-head motif in $T^t\text{BuPM}$ under isolated conditions has been proven by selectively probing the Raman-active central aliphatic C-D vibration within the dimer of the singly deuterated monomers. This arrangement is driven by London dispersion involving the *tert*-butyl groups which outbalances their steric repulsion. It is a first example of this binding motif investigated in an isolated dimer in the gas phase. In the unsubstituted TPM dimer no such dispersion interaction is possible, thus a tail-to-tail structure is identified as the most stable arrangement.

MO 12.5 Wed 11:30 S HS 002 Biologie

Nuclear-quadrupole coupling effects in laser alignment of asymmetric top molecules — •LINDA V. THESING^{1,2,3}, ANDREI DUCHKO^{1,3}, ANDREY YACHMENEV^{1,2}, ROSARIO GONZÁLEZ-FÉREZ⁴, and JOCHEN KÜPPER^{1,2,3,5} — ¹Center for Free-Electron Laser Science, DESY, Hamburg, Germany — ²Center for Ultrafast Imaging, Universität Hamburg, Germany — ³Department of Physics, Universität Hamburg, Germany — ⁴Instituto Carlos I and Departamento de Física Atómica, Molecular y Nuclear, Universidad de Granada, Spain — ⁵Department of Chemistry, Universität Hamburg, Germany

We present a theoretical time-dependent study of the field-free alignment of asymmetric top molecules taking into account the hyperfine coupling due to nuclear-quadrupole interactions. It was recently shown that the nuclear-quadrupole coupling influences the impulsive alignment of linear I_2 molecules on an experimentally relevant timescale [1]. Here, we analyze the field-free alignment dynamics, induced by a truncated laser pulse, for the prototypical iodobenzene and diiodobenzene molecules, unraveling the effects of the nuclear-quadrupole coupling. These theoretical studies illustrate how the coupling strength, the number of strongly coupled nuclei and rotational constants affect the alignment revival structure obtained for the different molecules.

[1] Thomas et al., *Phys. Rev. Lett.* **120**, 163202 (2018)

MO 12.6 Wed 11:45 S HS 002 Biologie
Rotational spectroscopy of molecular ions with 3×10^{-12} resolution and 1×10^{-10} precision — SOROOSH ALIGHANBARI¹, GOURI GIRI¹, FLORIN CONSTANTIN^{1,2}, MICHAEL HANSEN¹, VLADIMIR KOROBOV³, and ●STEPHAN SCHILLER¹ — ¹Heinrich-Heine-Univ. Düsseldorf — ²PhLAM, Univ. Lille, Villeneuve d'Ascq — ³Joint Inst. for Nucl. Research, Dubna

Trapped and sympathetically laser cooled molecular ions can be spectroscopied with high spectral resolution. So far, however, the achieved linewidths were limited by the residual Doppler broadening present even at the mK - level temperatures reached in traps. In the case of rotational spectroscopy, with its large transition wavelenghts, it is possible to take advantage of the confinement of the trapped ion ensemble in the directions transverse to the trap axis. It is then possible to reach the Lamb-Dicke regime, with a strong reduction in linewidth.

We demonstrate this on the molecular hydrogen ions HD⁺, whose fundamental rotational transition frequency is at 1.3 THz. We observe transition linewidths as small as 4 Hz. We fully resolve the hyperfine spectrum. We also measure the transition frequencies in absolute terms. We are then able to determine the precision of our technique by comparing the measured frequencies with the predictions from very accurate ab initio theory. We find agreement at the fractional level of 1×10^{-10} . This represents the most accurate comparison of a molecular physics prediction with experiment.

Finally, we measure some hyperfine energies with lower experimental uncertainty than the theoretical prediction.

MO 12.7 Wed 12:00 S HS 002 Biologie
Electronic Structure Theory for Molecular Precision Tests of New Physics — ●KONSTANTIN GAUL and ROBERT BERGER — Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein-Straße 4, 35032 Marburg, Germany

Detection of simultaneous violation of parity (\mathcal{P}) and time-reversal

(\mathcal{T}) symmetry can imply physics beyond the Standard Model of particle physics. Permanent electric dipole moments (EDMs) violate both \mathcal{P} - and \mathcal{T} -symmetry. EDMs of elementary particles or nuclei and \mathcal{P}, \mathcal{T} -odd electron-nucleus current interactions can induce a permanent EDM in atoms and molecules. Due to enormous electronic structure enhancements of \mathcal{P}, \mathcal{T} -odd effects in polar molecules, low-energy high-precision experiments on these molecules can give access to the TeV energy-regime. These precision tests are the most promising experiments for a first measurement of a permanent EDM the electron[1].

We discuss requirements of molecules for those high-precision measurements that aim to find new physics. Trends of \mathcal{P}, \mathcal{T} -violation within the periodic system of elements determined with quasi-relativistic calculations[2] are discussed and measurement models for disentanglement of sources of \mathcal{P}, \mathcal{T} -violation in molecules are presented[3]. Simple analytical models, which are gauged by *ab initio* calculations, help to choose promising molecules for future experiments.

[1] ACME collaboration, *Nature* **562**, 355 (2018).

[2] K. Gaul et. al., *J. Chem. Phys.* **147**, 014109 (2017).

[3] K. Gaul et. al., arXiv:1805.05494, arXiv:1811.05749.

MO 12.8 Wed 12:15 S HS 002 Biologie
The observation of non-adiabatic alignment of gas-phase molecules via an adapted opto-galvanic technique. — CHRISTIAN MATTHAEI^{1,2}, ●MATTHEW S. ROBINSON¹, and MARKUS GÜHR¹ — ¹Institut für Physik und Astronomie, Universität Potsdam, Potsdam, Germany — ²Current Address: Institut für Physikalische und Theoretische Chemie, Julius-Maximilians-Universität Würzburg, Germany

We have developed a new method for observing the non-adiabatic alignment of gas-phase molecules via an adapted opto-galvanic technique, in which the critical components of the detector are an oscilloscope and a 9V battery. In this talk I will discuss how we were able to observe the rotational wavepacket revivals of N₂ and O₂ molecules in a near-atmospheric pressure air mixture, after excitation by an ultrafast laser pulse, with high precision using this technique.

MO 13: Annual General Meeting of the Molecular Physics Division

Time: Wednesday 12:45–13:45

Location: S HS 001 Biologie

Annual General Meeting of the Molecular Physics Division

MO 14: Ultrafast Multidimensional and Control Approaches

Time: Wednesday 14:00–16:00

Location: S HS 001 Biologie

MO 14.1 Wed 14:00 S HS 001 Biologie
Probing Phosphate-Magnesium Ion Interactions in Water using Ultrafast 2D-IR spectroscopy — ●JAKOB SCHAUSS, FABIAN DAHMS, BENJAMIN P. FINGERHUT, and THOMAS ELSAESSER — Max Born Institute for Nonlinear Optics and Short-Pulse Spectroscopy, Berlin, Germany

Biomolecules are fundamentally affected by electric interactions with their surrounding solvent shell and the embedded ions. Mg²⁺-ions are known to play a vital role in stabilizing RNA geometries, yet the underlying interactions are mainly unresolved. To unravel microscopic couplings and dynamics, non-invasive molecular probes are required, such as the phosphate vibrations of the nucleic acid backbone.

We used femtosecond 2D-IR spectroscopy on the dimethylphosphate anion DMP⁻, an established model system of the DNA/RNA backbone, and were able to observe a distinct blue shift of the asymmetric stretch vibration $\nu_{as}(\text{PO}_2)^-$ when magnesium ions were added. Concomitant theoretical ab-initio simulations attribute this frequency shift to the formation of contact DMP⁻/Mg²⁺ ion pairs, providing a handle to distinguish site-bound and diffuse ions in biomolecular systems in future research.

MO 14.2 Wed 14:15 S HS 001 Biologie
Rapid coherent three-dimensional fluorescence spectroscopy disentangles quantum pathways of a molecular dianion — ●STEFAN MÜLLER¹, JULIAN LÜTTIG¹, LEI JI², JIE HAN³, MICHAEL MOOS⁵, TODD B. MARDER², UWE H. F. BUNZ⁴, ANDREAS DREUW³, CHRISTOPH LAMBERT⁵, and TOBIAS BRIXNER¹ — ¹Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am

Hubland, 97074 Würzburg — ²Institut für Anorganische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg — ³Physikalisch-Chemisches Institut, Universität Heidelberg, Im Neuenheimer Feld 205, 69120 Heidelberg — ⁴Organisch-Chemisches Institut, Universität Heidelberg, Im Neuenheimer Feld 270, 69120 Heidelberg — ⁵Institut für Organische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

We developed a rapid shot-to-shot operating single-beam setup for electronic three-dimensional (3D) spectroscopy that uses fluorescence as an observable [1]. With this, we systematically acquire various types of 3D spectra, including multiple-quantum coherences, simultaneously, background free, inherently phased and within a few minutes. This allows us to study systems of limited chemical stability, such as the dianion of TIPS-tetraazapentacene [2]. Using a 125-fold phase cycling scheme, we isolate multiple 3D spectra that provide rich information up to sixth order in perturbation theory, revealing electronic coupling, nuclear wavepacket dynamics, highly-excited states, and more.

[1] S. Draeger et al., *Opt. Express* **25**, 3259 (2017).

[2] L. Ji et al., *J. Am. Chem. Soc.* **139**, 15968-15976 (2017).

MO 14.3 Wed 14:30 S HS 001 Biologie
Signatures of dipole-dipole interaction in 2D-spectroscopic signals of atomic gases — ●BENEDIKT AMES, EDOARDO CARNIO, VYACHESLAV SHATOKHIN, and ANDREAS BUCHLEITNER — Physikalisches Institut, Albert-Ludwigs-Universität Freiburg

Recent experimental studies have revealed collective effects in 2D fluorescence spectra of dilute atomic gases. These signals persist

down to the lowest experimentally accessible densities on the order of 10^7 cm^{-3} [1]. Given the large interatomic distances in this regime, the exchange of transverse photons is expected to play a significant role in the dipole-dipole interaction.

In order to identify the dominant contributions to the latter, we investigate a model that includes the retarded interaction as mediated by the quantized field and as such is valid across all length scales. In a first approach, we study the time evolution of the system in a master equation formulation that has previously been applied to coherent backscattering in the double scattering regime [2]. Secondly, we treat the same system perturbatively in the atom-laser coupling. By varying the strength of the coupling, we establish conditions under which the master equation approach yields the same results as the perturbative calculation.

[1] L. Bruder, M. Binz, F. Stienkemeier, Phys. Rev. A **92**, 053412 (2015)

[2] V. Shatokhin, C. Müller, A. Buchleitner, Phys. Rev. A **73**, 063813 (2006)

MO 14.4 Wed 14:45 S HS 001 Biologie

Theoretical treatment of many-body signals in nonlinear phase-modulated spectroscopy — ●GHASSAN ABUMWIS and ALEXANDER EISFELD — MPIPKS, Dresden, Germany

Using nonlinear phase-modulated spectroscopy, strong many-body signals have been observed in very dilute atomic gases [1,2]. So far, a theoretical explanation of these unexpected strong signals is missing. By extending the theoretical treatment of [3] we provide a possible explanation of the measurements.

[1]Bruder et al, Phys. Rev. A 92, 053412 (2015)

[2]Bruder et al, Phys Chem Chem Phys,(2018)DOI:10.1039/c8cp05851b

[3]Li et al, Phys. Rev. A 95, 052509 (2017)

MO 14.5 Wed 15:00 S HS 001 Biologie

Excited state Rabi-cycling near the ionization threshold after multiphoton excitation - a general concept? — ●TOM RING, HENDRIKE BRAUN, ALEXANDER KASTNER, CONSTANTIN WITTE, HAN-GYEOL LEE, ARNE SENFTLEBEN, and THOMAS BAUMERT — Universität Kassel, Institut für Physik und CINSaT, 34132 Kassel, Germany

Control schemes using ultrashort laser pulses in the weak field regime such as the basic I^n behaviour and spectral interference as well as in the strong field regime such as Rabi-cycling, rapid adiabatic passage, photon locking or selective population of dressed states are well established. The excitation of molecules and atoms with near infrared femtosecond laser pulses can merge these regimes: In many cases the first excitation step is predominantly non-resonant (weak field interaction) while the increasing density of states near the ionization threshold results in the possibility of subsequent one-photon absorptions which can lead to excited state Rabi-cycling (strong field interaction).

To investigate coherent dynamics of atoms and molecules in this combination region we employ 2d strong field spectroscopy using sequences of phase modulated femtosecond laser pulses. Varying the relative optical phase and the temporal separation between adjacent pulses allows to look at the coherent response of the atomic level as well as molecular systems in the form of electronic coherences. Comparison of our experimental results with simulations confirms the subsequent weak and strong field behaviour.

MO 14.6 Wed 15:15 S HS 001 Biologie

Coherent control of two-photon absorption via entangled photons — ●EDOARDO CARNIO¹, FRANK SCHLAWIN², and ANDREAS BUCHLEITNER¹ — ¹Physikalisches Institut, Albert-Ludwigs Universität Freiburg, Germany — ²Clarendon Laboratory, University of Ox-

ford, United Kingdom

Coherent control exploits the coherence of classical light to drive an initial quantum state to a desired final state. In two-photon absorption (TPA), in particular, two photons are used to excite a molecule from the ground to an excited state. Under certain conditions, frequency-entangled photons drive the transition more efficiently than in the classical case [1]. We first show how this enhancement correlates with the entropy of entanglement of the two-photon state, both in the transient and in the steady states. We then extend our analysis to the case of a manifold of intermediate states, where we aim to control specific excitation pathways with the appropriate design of the two-photon states.

[1] Schlawin, F. & Buchleitner, A. *Theory of coherent control with quantum light*. New J. Phys. 19, 013009 (2017).

MO 14.7 Wed 15:30 S HS 001 Biologie

Phase control of complex Fano resonances — ●NICOLA MAYER, MISHA IVANOV, and OLEG KORNILOV — Max Born Institute, Max-Born-Straße 2A, 12489 Berlin, Germany.

Complex Fano resonances are quantum mechanical systems consisting of two or more discrete states coupled to one or more common continua. If the coupling strength to the continuum is comparable to the energy separation between discrete states, an increase of coupling strength leads to a counterintuitive increase of lifetime of one of the discrete states, while the lifetime of the other becomes shorter. This phenomenon is known as interference stabilization [1]. In a previous publication, we showed that this effect may occur in a complex autoionizing resonance in molecular nitrogen [2]. In this contribution, we explore the possibility of controlling the autoionization and population dynamics by using an auxiliary laser pulse. We develop a model for photoelectron experiments employing a three pulse scheme: an XUV pulse is used to excite the autoionizing states, a concomitant control NIR/VIS/UV pulse induces a relative phase shift between the autoionizing amplitudes and the resulting population dynamics is probed by a delayed NIR pulse. We show that depending on the relative phase induced by the control pulse, it is possible to selectively excite the long- or short-lived autoionizing states. Our results pave the way for future experiments where the control pulse sequences can be used both to steer the autoionization dynamics in the well-studied systems and applied as a spectroscopic tool to retrieve the intrinsic electron configuration interaction in unexplored systems.

MO 14.8 Wed 15:45 S HS 001 Biologie

Quantum Control with Quantum Light of Non-Adiabaticity in Molecules — ANDRÁS CSEHI¹, GÁBOR J. HALÁSZ¹, ÁGNES VIBÓK¹ und ●MARKUS KOWALEWSKI² — ¹Department of Theoretical Physics, University of Debrecen, H-40410 Debrecen, PO Box 5, Hungary — ²Department of Physics, AlbaNova University Center, Stockholm University, 10691 Stockholm, Sweden

Coherent control in molecules is usually done with laser fields. The electric field is described classically and control over the time evolution of the system is achieved by shaping the phase and amplitude of laser pulses in the time or frequency domain. Moving on from a classical description to a quantum description of the light field enables us to engineer the quantum state of light and allows to manipulate the light-matter interaction in phase space instead. In this paper we will demonstrate the different principles of control with quantum light on the avoided crossing in lithium fluoride. Using a quantum description of light together with the non-adiabatic couplings and vibronic degrees of freedoms opens up new ways to look at quantum control. We will show the deviations from control with purely classical light field and how back action of the light field becomes important in a few photon regime.

MO 15: Cold Molecules (joint session MO/A)

Time: Wednesday 14:00–16:00

Location: S HS 002 Biologie

MO 15.1 Wed 14:00 S HS 002 Biologie

Progress towards ultracold RbSr molecules in an optical lattice — ●VINCENT BARBÉ, LUKAS REICHSÖLLNER, SÉVERIN CHARPIGNON, KLAASJAN VAN DRUTEN, and FLORIAN SCHRECK — University van Amsterdam, Amsterdam, Netherlands

Our group recently reported on the observation of Feshbach resonances

between Rb and Sr atoms in an optical dipole trap [1], and on the experimental investigation of the Rb-Sr electronic ground-state interaction potential [2]. We will present our current efforts aimed at building an optical lattice system that supports a Rb-Sr double-Mott insulator with a high filling fraction, and a high magnetic-field stabilization system for magnetoassociation.

[1] V. Barbé, A. Ciamei, B. Pasquiou, L. Reichsöllner, F. Schreck, P. Zuchowski, and J. Hutson, *Nature Physics* **14**, 881-884 (2017)

[2] A. Ciamei, J. Szczepkowski, A. Bayerle, V. Barbé, L. Reichsöllner, S. M. Tzanova, C. C. Chen, B. Pasquiou, A. Grochola, P. Kowalczyk, W. Jastrzebski and F. Schreck, *Phys. Chem. Chem. Phys.*, **20**, 26221-26240 (2018)

MO 15.2 Wed 14:15 S HS 002 Biologie

Phase protection of Fano-Feshbach resonances — ALEXANDER BLECH¹, YUVAL SHAGAM², NICOLAS J. HÖLSCH², PRERNA PALIWAL², WOJCIECH SKOMOROWSKI¹, JOHN W. ROSENBERG², DANIEL ZAJFMAN³, ODED HEBER³, DANIEL M. REICH¹, EDVARDAS NAREVICIUS², and CHRISTIANE P. KOCH^{1,2} — ¹Theoretische Physik, Universität Kassel, Heinrich-Plett-Straße 40, 34132 Kassel, Germany — ²Department of Chemical Physics, Weizmann Institute of Science, Rehovot 76100, Israel — ³Department of Particle Physics and Astrophysics, Weizmann Institute of Science, Rehovot 76100, Israel

Fano-Feshbach resonances (FFR) describe the decay of a quantum system due to coupling of quantum-mechanical bound states to a continuum of scattering states. They serve as a key mechanism to controlling interactions in ultracold atomic gases. The position of FFR was shown to follow quantum chaotic statistics. In contrast, their lifetimes have so far escaped a similarly comprehensive understanding, despite the intriguing observation of spanning many orders of magnitude. We attribute this phenomenon, which has also been observed in predissociation FFR, to phase protection: For each scattering energy, there exists a phase for which the lifetime becomes infinite. Any bound state which is resonantly coupled to the scattering state with exactly this phase is phase protected. Supported by lifetime measurements of rovibrational FFR, we demonstrate that both the reduced mass and the shape of the potential can significantly influence the occurrence of phase-protected resonances. Our results provide a blueprint for identifying naturally long-lived states in a decaying quantum system.

MO 15.3 Wed 14:30 S HS 002 Biologie

The Dipolar Ground State of Ultracold LiK Molecules — SOFIA BOTSIS¹, ANBANG YANG¹, SUNIL KUMAR¹, and KAI DIECKMANN^{1,2} — ¹Centre for Quantum Technologies, 3 Science Drive 2, 117543 Singapore — ²Department of Physics, National University of Singapore, 2 Science Drive 3, 117542 Singapore

Ultracold polar molecules are an ideal tool for the quantum simulation of a large class of many-body effects, for quantum information processing, controlled ultracold chemistry, and quantum metrological applications. We report on our experiments that identified the ground state of bosonic heteronuclear dimers of ⁶Li and ⁴⁰K. In the ground state these molecules possess a large permanent electric dipole moment of 3.6 Debye, which makes them a suitable candidate for a quantum gas with long-range anisotropic dipole interaction. Starting from closed channel dominated Feshbach molecules we describe a new spectroscopy route to the ground state that is different from schemes previously used for other alkali heteronuclear dimers. Only strong transitions between molecular spin singlet states are involved avoiding the need to identify suitable perturbed triplet states. We demonstrate how only a sole hyperfine component can be addressed, even if the hyperfine structure is not resolved. Effectively creating a three level system the resulting scheme is the most straight forward to date and takes full advantage of the closed molecular channel that can be discussed by means of the simple asymptotic bound state model for our case. Further, we present results from rotational spectroscopy that facilitates to exploit the high electric dipole moment for use of the molecules as a quantum bit.

MO 15.4 Wed 14:45 S HS 002 Biologie

Ultracold ²³Na⁴⁰K Ground-State Molecules in a 3D Optical Lattice — MARCEL DUDA¹, ROMAN BAUSE¹, SCOTT EUSTICE¹, FRAUKE SEESSELBERG¹, XING-YAN CHEN¹, CHRISTOPH GOHLE¹, IMMANUEL BLOCH^{1,2}, and XIN-YU LUO¹ — ¹Max-Planck Institut für Quantenoptik, Hans-Kopfermann-Str. 1, 85748 Garching, Germany — ²Ludwig-Maximilians-Universität, Schellingstraße 4, 80799 München, Germany

Ultracold polar molecules represent an interesting platform to study quantum many-body physics. In contrast to atoms, molecules exhibit a rich rotational and vibrational structure. Additionally, ground-state molecules have a strong permanent electric dipole moment which allows the investigation of spin models beyond nearest-neighbor interactions. In this talk, we will report on the progress of creating a fermionic low entropy gas of ²³Na⁴⁰K ground-state molecules in a three-dimensional optical lattice.

After loading an ultracold mixture of ²³Na and ⁴⁰K atoms into the 3D lattice, we produce NaK molecules in the rotational-vibrational ground-state by associating Feshbach molecules from atoms followed by stimulated Raman adiabatic passage. We observe a significantly extended lifetime of NaK molecules in the 3D optical lattice and anticipate an improved Feshbach molecule association efficiency.

With sufficiently high filling and lifetimes of the ground-state NaK molecules in the 3D lattice, it is possible to observe intriguing spin dynamics such as condensate of rotational excitations or anisotropic propagation of spin waves.

MO 15.5 Wed 15:00 S HS 002 Biologie

Reaction and Spectroscopy Studies of Astrophysically relevant Anions in Multipole Traps — MARKUS NÖTZOLD, ROBERT WILD, MALCOLM SIMPSON, THOMAS ZURIN, and ROLAND WESTER — Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck, Austria

Multipole ion traps are versatile tools for the study of cold molecular ions. 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 (ISM). Our group has previously performed photodetachment studies on C_nH⁻ [1], CN⁻ and C₃N⁻ anions [2], and recently begun to study the three-body recombination mechanism H₂ + H⁻ + X ⇒ H₃⁻ + X. We report on progress and the current status of these experiments. In addition to the foregoing, our group is currently developing a new multipole wire trap for our setup. We present the main features of this improvement compared to our existing 22-pole trap.

[1] T. Best, R. Otto, S. Trippel, P. Hlavenka, A. von Zastrow, S. Eisenbach, S. Jézouin, R. Wester, E. Vigrén, 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).

MO 15.6 Wed 15:15 S HS 002 Biologie

A Cold and Slow Molecular Beam of Barium Monofluoride — RALF ALBRECHT, MICHAEL SCHARWAECHTER, TOBIAS SIXT, and TIM LANGEN — 5. Physikalisches Institut and Center for Integrated Quantum Science and Technology IQST, Universität Stuttgart

We report on our progress towards the direct 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.

In our experiment, molecules are generated through laser ablation of a sintered precursor target inside a cryogenic cell. Subsequently, the initially ~ 10⁴ K hot molecules are precooled to the few Kelvin regime by collisions with a cold buffer gas of helium atoms. The precooled molecules exit the cell through a millimeter-sized aperture and enter a room-temperature high-vacuum region, where they form a cold and intense molecular beam. We present measurements characterizing this beam using laser-induced fluorescence and outline our strategy for future laser cooling.

MO 15.7 Wed 15:30 S HS 002 Biologie

Cold beam of water dimer — HELEN BIEKER^{1,2,4}, JOLIJA ONVLEE¹, MELBY JOHNY¹, LANHAI HE^{1,5}, THOMAS KIERSPEL^{1,2,4}, BORIS SARTAKOV³, ANDREY YACHEMENEV¹, SEBASTIAN TRIPPEL^{1,3}, DANIEL A. HORKE^{1,2}, and JOCHEN KÜPPER^{1,2,4} — ¹Center for Free-Electron Laser Science, DESY — ²The Hamburg Center for Ultrafast Imaging, University Hamburg — ³General Physics Institute, Russian Academy of Sciences — ⁴Department of Physics, University of Hamburg — ⁵Institute of Atomic and Molecular Physics, Jilin University, Changchun, China

To unravel the microscopic details of intermolecular interactions in water, we prepared controlled samples of size- and isomer-selected water clusters. Inhomogeneous electric fields allowed 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, extending previous studies.

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

MO 15.8 Wed 15:45 S HS 002 Biologie
Manipulation of molecular hydrogen on a chip to study cold collisions with a merged beam apparatus — ●KATHARINA HÖVELER¹, JOHANNES DEIGLMAYR², PITT ALLMENDINGER¹, JOSEF AGNER¹, HANSJÜRGEN SCHMUTZ¹, and FRÉDÉRIC MERKT¹ — ¹Laboratorium für Physikalische Chemie, ETH Zürich, 8093 Zurich, Switzerland — ²Felix-Bloch Institut, Universität Leipzig, Linnéstraße 5, 04103 Leipzig, Germany

The exothermic, barrierless $\text{H}_2^+ + \text{H}_2 \rightarrow \text{H}_3^+ + \text{H}$ reaction has been studied in the collision-energy range $E_{\text{coll}}/k_{\text{b}} = 0.3 - 50$ K. To reach such low collision energies, we use a merged-beam approach and substitute the H_2^+ reactants by the ionic cores of H_2 molecules in high- n Rydberg-Stark states. The Rydberg electron does not influence the reaction but

shields the ion from heating by space-charge effects and stray electric fields. A curved surface-electrode device is used to deflect a supersonic beam of H_2 molecules excited to high- n Rydberg-Stark states and to merge it with a supersonic beam containing ground-state H_2 molecules. The collision energy is tuned by varying the temperature of the valve generating the H_2 ground-state beam for selected velocities of the deflected H_2 beam. The reaction cross section is found to follow the classical Langevin capture model down to $E_{\text{coll}}/k_{\text{b}} = 5$ K. At lower temperatures, a deviation is observed and attributed to ion-quadrupole long-range interactions. Investigation of the reaction $\text{H}_2^+ + \text{D}_2$ enables us to distinguish between charge transfer, D atom transfer and H^+ ion transfer and to determine the ratio of the two competing reaction channels leading to the product ions H_2D^+ and D_2H^+ .

MO 16: Cluster I (joint session A/MO)

Time: Wednesday 14:00–16:15

Location: S HS 3 Physik

Invited Talk MO 16.1 Wed 14:00 S HS 3 Physik
Imaging ultrafast dynamics in nanoparticles with resonant multicolor XUV pulses — L HECHT², B LANGBEHN², J ZIMMERMANN¹, J JORDAN², K KOLATZKI¹, N MONSERUD¹, Y OVCHARENKO³, M SAUPPE¹, B SCHÜTTE¹, R TANYAG¹, A ULMER², B KRUSE⁴, K SANDER⁴, C PELTZ⁴, A COLOMBO⁵, A D'ELIA⁶, M DI'RAIA⁷, L GIANNESI⁷, P PISERI⁵, O PLEKAN⁷, K PRINCE⁷, M ZANGRANDO⁷, C CALLEGARI⁷, MJJ VRAKING¹, A ROUZÉE¹, T MÖLLER², T FENNEL², and ●D RUPP¹ — ¹MBI Berlin, Germany — ²TU Berlin, Germany — ³E-XFEL, Schenefeld, Germany — ⁴Uni Rostock, Germany — ⁵Uni Milano, Italy — ⁶Uni Trieste, Italy — ⁷Elettra, Trieste, Italy

Diffraction imaging with intense, coherent, short-wavelength light pulses is a unique method to determine the structure of individual nanometer-sized objects such as viruses or fragile superfluid helium nanodroplets. In addition, diffraction imaging can be also used as a probe for ultrafast electronic processes within the particle. As the photons are elastically scattered by the electrons bound to the particle, the scattering response will be altered if the particle's electronic structure changes, with particularly strong effects at electronic resonances. In two experiments we employed this concept using extreme ultraviolet (XUV) multicolor pulses from an intense high-harmonic generation source and two-color pulses from the FERMI free-electron laser, respectively, to resonantly image helium nanodroplets and trace light induced excitation and ionization processes within them.

Invited Talk MO 16.2 Wed 14:30 S HS 3 Physik
Multi-coincidence experiments on electron and photon emission — ●ANDRE KNIE — Institut für Physik und CINSaT, Universität Kassel

The coincident detection of particles is a powerful method in experimental physics, enabling the reconstruction of diverse projectile-target interactions. The overwhelming majority of coincidence experiments is performed detecting exclusively charged particles. When neutrals or photons are of interest, experiments typically suffer from small solid angles. Here, a new approach is shown maximizing the available solid angle for photon detection, confining the interaction volume within focusing optics. With it a series of experiments was performed on atomic and cluster samples to underline its capabilities. With this technique it was possible to disentangle Auger processes in argon otherwise unresolvable by spectroscopic means. Additionally, the coincident detection was used to circumvent the typical signal to noise ratio of an ultra low cross section process, e.g. luminescent shake up satellites in helium. The final example shows that completely new processes can be unraveled with this technique: A new energy transfer process in weakly bound heterogeneous noble gas clusters will be presented.

MO 16.3 Wed 15:00 S HS 3 Physik
Auger Emission from the Coulomb Explosion of Helium Nanoplasmas — ●MICHAEL ZABEL, MICHAEL KELBG, BENNET KREBS, JOSEF TIGGESBÄUMKER, and KARL-HEINZ MEIWES-BROER — Universität Rostock, Institut für Physik, Albert-Einstein-Strasse 23-24, 18059 Rostock

The long-time correlated decay dynamics of strong-field exposed helium nanodroplets is studied by means of angular resolved electron spectroscopy. As a result of the adiabatic expansion of the fully ion-

ized plasma, delocalized electrons in the laser-produced deep confining mean field potential are shifted towards the vacuum level, whereas some electrons may localize in bound levels of the helium ion. The simple hydrogen-like electronic structure of He^+ results in clear signatures in the experimental electron spectra. The pronounced features in the electron yields can be traced back to bound-free and bound-bound transitions in He^+ . Auger electron emission takes place as a result of the transfer of the excess energy to weakly bound electrons in the quasifree electron band. Hence, the spacial and temporal development of the nanoplasma cloud is encoded in the experimental spectra, whereas the special electronic properties of helium helps to clearly resolve the different contributions.

MO 16.4 Wed 15:15 S HS 3 Physik
Plasmon resonances of polyanionic metal clusters — ●KLARA RASPE¹, NORMAN IWE¹, MADLEN MÜLLER², FRANKLIN MARTINEZ¹, JOSEF TIGGESBÄUMKER¹, LUTZ SCHWEIKHARD², and KARL-HEINZ MEIWES-BROER¹ — ¹Institut für Physik, Universität Rostock, Albert-Einstein-Str. 23-24, 18059 Rostock — ²Institut für Physik, Universität Greifswald, Felix-Hausdorff-Str. 6, 17489 Greifswald

In the interaction of metal clusters with light the occurrence of plasmon resonances is a well known effect. We present photoelectron spectra of negatively charged silver clusters which indicate such a plasmon resonance, and - in the case of higher charge states - show also the Coulomb Cut-Off. In this contribution we discuss the plasmon energies with respect to well-defined cluster sizes and charge states and compare them to literature values of smaller silver clusters. The project has been supported by the collaborative research center SFB 652 of the DFG.

MO 16.5 Wed 15:30 S HS 3 Physik
Time-resolved coherent diffraction imaging of helium nanodroplets in free flight with intense high-harmonic XUV-pulses — ●J ZIMMERMANN¹, K. KOLATZKI¹, N. MONSERUD¹, M. SAUPPE¹, B. SCHÜTTE¹, R. M. TANYAG¹, M.J.J. VRAKING¹, A. ROUZÉE¹, J. JORDAN², B. LANGBEHN², A. ULMER², T. MÖLLER², B. KRUSE³, T. FENNEL³, and D. RUPP¹ — ¹MBI Berlin — ²IOAP, TU Berlin — ³Univ. Rostock

Coherent diffraction imaging (CDI) of single particles in free flight enables studying the structural composition of fragile nano-scaled matter. Such experiments demand high-intensity extreme ultraviolet or X-ray light pulses, until recently only achievable at large-scale free-electron laser (FEL) facilities. We have demonstrated [1] that high harmonic generation (HHG) sources can be used for single-shot single-particle CDI with great prospects for time-resolved experiments due to high stability and extremely short pulse durations. Here we report on the first time-resolved CDI measurements using a HHG laser system on helium nanodroplets in an IR pump - XUV probe scheme. We obtained bright multicolor diffraction patterns in a setup that allowed for few femtoseconds time-resolution. First results of the ongoing analysis will be presented and discussed. [1] Rupp et al., Nat.Com.8,493(2017)

MO 16.6 Wed 15:45 S HS 3 Physik
Investigation of polyanionic metal clusters by photoelectron spectroscopy — ●MADLEN MÜLLER¹, FRANKLIN MARTINEZ², NORMAN IWE², KLARA RASPE², STEFFI BANDELOW¹, JOSEF TIGGESBÄUMKER², LUTZ SCHWEIKHARD¹, and KARL-HEINZ MEIWES-

BROER² — ¹Institute of Physics, University of Greifswald, Germany
— ²Institute of Physics, University of Rostock, Germany

One of the most prominent features of polyanionic systems is the Coulomb barrier (CB), already confirmed by photoelectron spectroscopy (PES) on molecules and fullerenes. Recently such studies have been extended to the field of polyanionic metal clusters. While offering a variety of sizes and charge states to analyze, metal clusters also serve as model systems with a simplified access e.g. by the liquid drop model (LDM).

The contribution presents an overview of our measurements on polyanionic metal clusters. The study includes the determination of threshold binding energies, that support the LDM along a wide range of cluster sizes and extending to negative binding energies. Furthermore, multiphoton processes and the Coulomb cut-off dominate the structure of the PE spectra. In particular, the evolution of the Coulomb cut-off with charge state and cluster size leads to further insights into the nature of the Coulomb barrier. The project has been funded by the collaborative research center SFB 652 of DFG.

MO 16.7 Wed 16:00 S HS 3 Physik

Ultrafast Ionization Dynamics of Methane Clusters — ●A. HEILRATH¹, M. SAUPPE^{1,2}, K. KOLATZKI^{1,2}, B. LANGBEHN¹, B.

SENFITTEBEN², A. ULMER¹, J. ZIMMERMANN^{1,2}, L. FLÜCKIGER³, T. GORKHOVER⁴, C. BOSTEDT⁵, Y. KUMAGAI⁶, S. DÜSTERER⁷, B. ERK⁷, C. PASSOW⁷, D. RAMM⁷, D. ROLLES^{7,8}, D. ROMPOTIS⁷, R. TREUSCH⁷, T. FEIGL⁹, T. MÖLLER¹, and D. RUPP^{1,2} — ¹Technische Universität Berlin — ²Max-Born-Institut, Berlin — ³La Trobe University, Australia — ⁴SLAC Menlo Park, USA — ⁵Paul Scherrer Institut, Switzerland — ⁶Argonne National Lab, USA — ⁷FLASH@DESY — ⁸Kansas State University, USA — ⁹optiX fab, Jena

Intense short wavelength femtosecond pulses from free-electron lasers (FELs) allow to study individual nanoparticles with high resolution in time and space. Exposing samples to intense extreme ultraviolet (XUV) pulses is inevitably linked to ionization and subsequent disintegration of the sample, limiting the accuracy of diffraction imaging. Molecular clusters are an ideal sample system to approach light-induced dynamics of large heteronuclear systems. We studied methane clusters in an XUV pump - XUV probe experiment with 90 eV photon energy at CAMP@FLASH with delays up to 650 ps. Ionic fragments were measured with a time-of-flight spectrometer and diffraction images were taken simultaneously. The ion spectra exhibit a variety of fragments, including higher adducts forming in molecular recombination processes. A general increase of the ion yield with delay as well as the delay-dependencies of fragments will be discussed.

MO 17: Cluster II (joint session A/MO)

Time: Wednesday 16:15–18:15

Location: S Fobau Physik

MO 17.1 Wed 16:15 S Fobau Physik

Investigation of 2p Auger decay in argon clusters by electron-electron and electron-photon coincidences — ●CATMARNA KÜSTNER-WETEKAM¹, PHILIPP SCHMIDT¹, CHRISTIAN OZGA¹, HUDA OTTO¹, ARNO EHRESMANN¹, UWE HERGENHAHN^{2,3}, ANDRÉ KNIE¹, and ANDREAS HANS¹ — ¹Institut für Physik und CINsAT, Universität Kassel, Heinrich-Plett-Str. 40, 34132 Kassel, Germany — ²Max Planck Institute for Plasma Physics Wendelsteinstr. 1, 17491 Greifswald, Germany — ³Leibniz Institute of Surface Modification, Permoserstr. 15, 04318 Leipzig, Germany

The response of prototype systems to ionizing soft X-ray irradiation is of crucial interest for the study of fundamental processes in radiation chemistry. Here we investigate Auger processes following 2p inner-shell ionization of argon atoms and clusters and discuss differences in the spectra of the atomic and the condensed sample. These Auger processes are important for the population of the initial states of various interatomic processes such as the Interatomic Coulombic Decay (ICD) and Radiative Charge Transfer (RCT). The coincident measurement of two electrons or one electron and one photon makes it possible to gain new insights into these processes.

MO 17.2 Wed 16:15 S Fobau Physik

Modular He nanodroplet source and doping setup for the SQS instrument at the European XFEL — ●ANATOLI ULMER¹, RICO MAYRO P. TANYAG^{1,2}, KATHARINA KOLATZKI^{1,2}, GEORG NOFFZ¹, PATRICK BEHRENS¹, FABIAN SEEL¹, BRUNO LANGBEHN¹, MARIO SAUPPE², YEVHENIY OVCHARENKO³, DANIELA RUPP², and THOMAS MÖLLER¹ — ¹Technische Universität Berlin — ²Max-Born-Institut Berlin — ³European XFEL GmbH

Ultra-cold helium nanodroplets gain growing attention in many fields, which can be attributed to their fascinating properties: they are superfluid, form quantized vortices and can be doped with various atomic or molecular samples. With the advance of Free-Electron Lasers (FEL), it has become feasible to determine the outer shapes as well as the structures of embedded nanometer-sized samples by using flash X-ray imaging. This opens a variety of experimental roads, such as cluster growth in a superfluid environment, using different droplet sizes, shapes and dopants. We developed a modular source and doping setup, which will be permanently available for user experiments at the SQS instrument of the European XFEL. A wide range of experiments will be enabled by using either an Even-Lavie Valve, a commercial Parker Valve, or a continuous jet nozzle. Furthermore, a doping system, consisting of a gas cell and two metal ovens, was designed to explore the formation and interaction of structures nested inside superfluid He droplets. The layout and characterization measurements of the setup will be presented.

MO 17.3 Wed 16:15 S Fobau Physik

Time-resolved imaging of the dynamics of free metal clusters and nanocrystals — I. BARKE³, N. BERNHARDT², P. BEHRENS², ●S. DOLD¹, S. DÜSTERER⁴, B. ERK⁴, T. FENNEL^{3,5}, H. HARTMANN³, L. HECHT², A. HEILRATH², R. IRSIG³, B. V. ISSENDORFF¹, N. IWE³, J. JORDAN², B. KRUSE³, B. LANGBEHN², B. MANSCHWETUS⁴, F. MARTINEZ³, K.-H. MEIWES-BROER³, T. MÖLLER², K. OLDENBURG³, C. PASSOW⁴, C. PELTZ³, D. RUPP^{2,5}, F. SEEL^{2,5}, R. TANYAG⁵, R. TREUSCH⁴, A. ULMER², and S. WALZ² — ¹Univ. Freiburg — ²TU Berlin — ³Univ. Rostock — ⁴FLASH@DESY — ⁵MBI Berlin

Wide angle X-Ray diffraction has been proven a viable tool to determine the 3D structure of single metal clusters in gas phase with a single X-Ray Pulse. We utilize the fs X-Ray pulses at the FLASH Free-Electron Laser in Hamburg to resolve ultrafast processes in metal clusters by reconstructing their shape in a time-dependent manner and simultaneous time-of-flight spectrometry of the ionic fragments. Exploiting the plasmon resonance of silver nanoparticles we use optical picosecond-second laser pulses to efficiently pump their electronic system. Picoseconds later we retrieve the resulting shape of the cluster. For moderate pumping energies (0.5 eV/Atom) we expect so see melting effects, whereas high energy input leads to the formation of a nanoplasma and disintegration of the cluster. To meet the demanding requirements for such experiments a carefully tailored source for clusters was developed. This source as well as a novel optical cluster detector will be presented and an overview of preliminary results from our recent experiments at FLASH will be given.

MO 17.4 Wed 16:15 S Fobau Physik

Correlation method for velocity map imaging of electrons and time-of-flight detection of ions emitted by individual mid-IR induced helium nanoplasmas. — ●CRISTIAN MEDINA¹, DOMINIK SCHOMAS¹, MARCEL MUDRICH³, MARCUS DEBATIN¹, FRANK STIENKEMEIER¹, ROBERT MOSHAMMER², and THOMAS PFEIFER² — ¹Albert-Ludwigs-University of Freiburg, Freiburg im Breisgau, Germany — ²Max plank Institute for nuclear physics, HEIDELBERG, GERMANY — ³Aarhus University, Aarhus, Denmark

Velocity map imaging (VMI) and time-of-flight (TOF) are standard techniques to probe the photodynamics of molecules and clusters. Using a combined VMI-TOF setup, we study nanoplasmas created from doped helium nanodroplets irradiated with intense mid-infrared femtosecond laser pulses. Quasi-free electrons created by tunnel ionization couple very efficiently to the laser field, thereby acquiring high energy and resulting in an avalanche of impact ionization. The large number of charged particles emitted from a single helium nanoplasma allows us to collect both full electron energy distributions (VMI) and ion mass-over-charge distributions (TOF) from a single hit. Our technique relies on linking the camera used for VMI to the oscilloscope that measures

TOF spectra. We discuss the impact of doping the He nanodroplets with various species (Xe, Ca and H₂O) to trigger the nanoplasma formation.

MO 17.5 Wed 16:15 S Fobau Physik

Coherent diffractive imaging of excited state population dynamics in a helium droplet — ●BJÖRN KRUSE¹, BENJAMIN LIEWEHR¹, CHRISTIAN PELTZ¹, and THOMAS FENNEL^{1,2} — ¹University of Rostock, Albert-Einstein-Straße 23, D-18059 Rostock — ²Max-Born-Institute, Max-Born-Straße 2A, D-12489 Berlin

Just recently, coherent diffractive imaging (CDI) of isolated helium nanodroplets has been successfully demonstrated with a lab-based HHG source [1] operating in the vicinity of the 1s - 2p transition of helium. To reconstruct the shape and orientation of nanoparticles, CDI experiments have so far been analyzed in terms of a classical linear response description [2]. However, for high intensities and especially for resonant excitation, population dynamics of bound electrons and stimulated emissions may become important, violating the assumptions underlying a linear description. To what extent and how nonlinear processes 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 the spatio-temporal population dynamics and its impact on scattering images in both single-shot and pump-probe scenarios.

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

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

MO 17.6 Wed 16:15 S Fobau Physik

Coulomb interaction in the photoemission of polyanionic silver clusters — ●NORMAN IWE¹, MADLEN MÜLLER², KLARA RASPE¹, FRANKLIN MARTINEZ¹, STEFFI BANDELOW², JOSEF TIGGESBÄUMKER¹, LUTZ SCHWEIKHARD², and KARL-HEINZ MEIWES-BROER¹ — ¹Institut für Physik, Universität Rostock, Albert-Einstein-Str. 23-24, 18059 Rostock — ²Institut für Physik, Universität Greifswald, Felix-Hausdorff-Str. 6, 17489 Greifswald

Not only the size but also the charge state is an important parameter of free, nanoscopic particles. In particular the properties of negatively charged metal clusters are strongly influenced by Coulomb interaction between the cluster components. For two and more excess electrons, this results in a Coulomb barrier potential, whose detailed properties are however largely unknown.

This contribution presents photoelectron spectroscopy studies on mass separated silver clusters, after they have been multiply negatively charged in a radiofrequency ion trap. The emitted electron interacts with the still negatively charged cluster which leads to a Coulomb cut-off, as known from molecular anions. To investigate this effect, PE spectra for different photon energies are compared. These spectra are qualitatively described by electrons coming from a Fermi distribution in a Jellium-like potential that either overcome or tunnel through the Coulomb barrier. The project has been supported by the collaborative research center SFB 652 of the DFG.

MO 17.7 Wed 16:15 S Fobau Physik

Time-resolved X-ray imaging of Anisotropic Nanoplasma Expansion — ●CHRISTIAN PELTZ¹, CHRISTOPH BOSTEDT², MATHIAS KLING³, THOMAS BRABEC⁴, ECKART RUEHL⁵, ARTEM RUDENKO⁶, TAIS GORKHOVER⁷, and THOMAS FENNEL¹ — ¹Institute of Physics, University of Rostock, Germany — ²Paul Scherrer Institute, Villigen, Switzerland — ³Faculty of Physics, LMU Munich, Germany — ⁴Department of Physics and Centre for Photonics Research, University of Ottawa, Canada — ⁵Physical Chemistry, FU Berlin, Germany — ⁶Department of Physics, Kansas-State University, USA — ⁷LCLS, SLAC National Accelerator Laboratory, Menlo Park, USA

We investigate the time-dependent evolution of laser-heated solid-density nanoparticles via coherent diffractive x-ray imaging, theoretically and experimentally. Our microscopic particle-in-cell calculations for R = 25 nm hydrogen clusters reveal that infrared laser excitation induces continuous ion ablation on the cluster surface. This process generates an anisotropic nanoplasma expansion that can be accurately described by a simple self-similar radial density profile. Its time evolution can be reconstructed precisely by fitting the time-resolved scattering images using a simplified scattering model in Born approximation [1]. Here we present the first successful high resolution reconstruction of corresponding experimental results, obtained at the LCLS

facility with SiO₂ nanoparticles (D=120 nm), giving unprecedented insight into the spatio-temporal evolution of laser-driven nanoplasma expansion.

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

MO 17.8 Wed 16:15 S Fobau Physik

Characterisation of a doping oven for embedding metals in helium droplets for the SQS instrument at the European XFEL — ●GEORG NOFFZ¹, ANATOLI ULMER¹, RICO MAYRO TANYAG^{1,2}, KATHARINA KOLATZKI^{1,2}, DANIELA RUPP^{1,2}, YEVHENIY OVCHARENKO³, and THOMAS MÖLLER¹ — ¹IOAP, Technische Universität Berlin, Germany — ²MBI, Berlin, Germany — ³European XFEL, Hamburg, Germany

One of the most fascinating applications of the European XFEL is the study of nanostructures by means of scattering experiments using ultra-short and extremely intense X-ray pulses. A challenge in these experiments is the loss of phase information needed for image reconstructions in order to make statements about the morphology of the diffracting object. The Droplet Coherent Diffractive Imaging (DCDI) [Struct. Dyn. **2**, 051102 (2015)] technique provides a fast method for retrieving phase information of nanostructures, such as clusters grown in helium droplets. In this case, the droplet serves as a reference object and as a container. This poster deals with the design and characterisation of a doping oven for embedding metals in helium droplets for an approved XFEL beamtime. Quadrupole mass analyzer and time-of-flight mass spectrometer measurements are performed for the investigation of the doping process. Furthermore, the structures of the embedded metals are deposited and afterwards investigated by transmission electron microscopy. This setup will be available at the SQS instrument at the European XFEL. In a final beamtime nanostructure formation in the droplets will be investigated.

MO 17.9 Wed 16:15 S Fobau Physik

Setup and characterization of a helium liquid jet for diffractive imaging experiments — ●KATHARINA KOLATZKI^{1,2}, RICO MAYRO P. TANYAG^{1,2}, GEORG NOFFZ², ANATOLI ULMER², DANIELA RUPP^{1,2}, and THOMAS MÖLLER² — ¹MBI, Germany — ²IOAP TU Berlin, Germany

State-of-the-art XUV and X-ray facilities like high-harmonic generation sources and free-electron lasers enable the in-depth investigation of light-matter interaction via novel methods such as single-particle coherent diffractive imaging.

For such experiments, large helium droplets constitute a suitable target; they have a simple electronic structure and exhibit interesting properties like superfluidity. One way of creating these droplets is a helium liquid jet, which disintegrates in a Rayleigh-type breakup, forming large droplets with diameters of a few microns. Compared to the other regimes of helium droplet generation, droplets produced from jet disintegration have a narrower size distribution. This makes them eligible for time-resolved diffractive imaging experiments, where a reproducible target is indispensable.

Recently, we have constructed and characterized a source for a helium liquid jet, which will be put into use for example at the SQS endstation at the European XFEL. Via shadowgraphy methods, we can analyze the jet's shape and the droplet size. Complementary, our setup allows to determine the average droplet size via collision with external gas particles. First results will be presented.

MO 17.10 Wed 16:15 S Fobau Physik

Direct evidence of radiative charge transfer in heterogeneous noble gas clusters — ●XAVIER HOLZAPFEL¹, ANDREAS HANS¹, CHRISTIAN OZGA¹, VASILI STUMPF², HUDA OTTO¹, CATMARNA KÜSTNER-WETEKAM¹, ARNO EHRESMANN¹, and ANDRÉ KNIE¹ — ¹Institut für Physik und CINSA^T, Universität Kassel, Heinrich-Plett-Str. 40, 34132 Kassel, Germany — ²Physikalisch-Chemisches Institut, Universität Heidelberg, Im Neuenheimer Feld 229, 69120 Heidelberg, Germany

Weakly bound noble gas clusters are artificial systems which can be used for the understanding of non-local energy transfer processes. In the case of the so called radiative charge transfer (RCT) the system can relax by redistributing the charges by emitting the excessive energy as a photon. Therefore, these photons can be used as a fingerprint of the electronic structure of the system if they are measured energy resolved. Here we present the direct observation of (RCT) in heterogeneous NeKr and NeXe clusters by dispersed ultravioletphoton detection.

MO 18: Posters 2: Time Resolved Spectroscopy

Time: Wednesday 16:15–18:15

Location: S Foyer LLM

MO 18.1 Wed 16:15 S Foyer LLM

Time-Resolved step-scan FTIR investigations of luminescent first row transition metal complexes — ●PIT BODEN¹, PATRICK DI MARTINO-FUMO¹, SVEN OTTO², MATTHIAS DORN², CLAUDIA BIZZARRI³, KATJA HEINZE², and MARKUS GERHARDS¹ — ¹Physical Chemistry, TU Kaiserslautern, Germany — ²Inorganic Chemistry and Analytical Chemistry, JGU Mainz, Germany — ³Organic Chemistry, KIT, Germany

In this contribution, the time-resolved step-scan FTIR technique is used for investigations of highly luminescent first row transition metal complexes in their electronically excited states with lifetimes in the microsecond regime. The vibrational frequencies obtained from this technique, compared with theoretical calculations, allow for a structural assignment of the excited states. The chosen molecular systems include a series of mononuclear Cr³⁺-complexes with dipyrindium ligands. These NIR-emitting complexes have a very high luminescence quantum yield and two energetically close lying doublet states, where the relative population can be influenced by cooling down a solid sample to at least 20 K or by applying the newly developed double resonance techniques. The analysis is extended to a related V³⁺-complex. Additionally, a photosensitive mononuclear Cu(I)-complex and its bridged binuclear analogue are investigated. By comparison with theoretical results, the structures of the electronic ground and lowest lying electronically excited state are determined.

MO 18.2 Wed 16:15 S Foyer LLM

Photodynamics of an Iron-based Photosensitizer after Deep-UV Excitation — ●NIKLAS GESSNER¹, LION-LUCA STIEWE¹, JOHANNES MOLL², KATJA HEINZE², and PATRICK NUERNBERGER¹ — ¹Physikalische Chemie II, Ruhr-Universität Bochum, 44801 Bochum — ²Institute of Inorganic Chemistry and Analytical Chemistry, Johannes Gutenberg University Mainz, 55128 Mainz

Photosensitizers are capable of transferring their energy to adjacent molecules after photoexcitation. However, many compounds used in this way in medicine or photovoltaics are complexes of rare noble metals. In contrast to this, [Fe(cpmp)₂]²⁺ comprises an earth-abundant central iron atom that may significantly reduce costs.

In this contribution, we study its photochemical properties with transient absorption spectroscopy in the ultraviolet, visible and mid-infrared (MIR) after excitation at 280 nm to a highly energetic state. Initially, [Fe(cpmp)₂]²⁺ exhibits dynamics on a timescale of 10 ps associated with vibrational cooling and rapid relaxation to a long-lived excited state which shows an excited-state absorption (ESA) around 320 nm. Subsequently, this ESA, the MIR signatures as well as the ground-state bleach decay with the same untypically short time constant of ≈540 ps. In accordance with related compounds [1,2], the study discloses that [Fe(cpmp)₂]²⁺ belongs to the recently emerging class of iron(II) compounds with a strong ligand field so that the system reaches a long-lived ³MC (metal centered) state.

[1] L. L. Jamula *et al.*, *Inorg. Chem.* **53**, 15-17 (2014).[2] A. K. C. Mengel *et al.*, *Chem. Eur. J.* **21**, 704-714 (2015).

MO 18.3 Wed 16:15 S Foyer LLM

Spin-flip dynamics in transition metal complexes triggered by soft X-ray light — ●VLADISLAV KOCHETOV, HUIHUI WANG, and SERGEI BOKAREV — Institut für Physik, Universität Rostock, 18059 Rostock

The prominent development of intense X-ray laser technologies stimulates theoretical studies of phenomena occurring at ultra-short timescales. Time-resolved experiments revealing the energy and charge transfer effects in molecular systems are of great importance. Here we present the investigation of spin-flip dynamics of an iron complex triggered by short X-ray pulses. The process of core excitation and consecutive changes in spin populations are simulated and analyzed in terms of density matrix within the time-dependent restricted active space configuration interaction theory. Calculations take into account the nuclear motion as a vibrational bath and Auger decay via quantum master equation in the Markov approximation. The detailed analysis of spin population distributions evolving during the first femtoseconds after excitation is presented and the role of electron correlation in the spin-flip process is discussed in the current work. Also, the influence of different ligands and various pulse characteristics on the initiated dy-

namics is demonstrated suggesting the design of possible experiments and applications in spintronics.

MO 18.4 Wed 16:15 S Foyer LLM

Cooperative effects in Ir, Pt and Pd containing bimetallic complexes — ●TATJANA WALL¹, MARKO LEIST², WERNER R. THIEL², and MARKUS GERHARDS¹ — ¹Physical Chemistry, TU Kaiserslautern — ²Inorganic Chemistry, TU Kaiserslautern

Bimetallic complexes can show cooperative effects between the metal centers that can influence spectroscopic properties as well as their performance in catalysis. To investigate such effects, absorption and emission spectra of a homologous series of mono- and binuclear transition metal complexes based on (2-dimethylamino)-4-(2-pyrimidinyl)pyrimidine in different solvents were recorded. Furthermore the lifetimes of the excited states were determined by using the time correlated single photon counting (TCSPC) method. Here we represent the results for Ir, Pt and Pd containing complexes. The results are compared with the pure ligand and additionally a comparison with DFT calculations is performed. For both types of complexes, mono- as well as binuclear ones, MLCT (Metal to Ligand Charge Transfer) and ligand centered bands are observed. The shifts of these bands compared to the pure ligand give information about cooperative effects. Lifetime determinations show multiple exponential decays for both emission bands, whereas the pure ligand has a mono-exponential decay. The photophysics of complexes with respect to lifetimes, coordinations and characters of electronically excited states are discussed.

MO 18.5 Wed 16:15 S Foyer LLM

Mapping of exciton-exciton annihilation in a molecular dimer via fifth-order femtosecond two-dimensional spectroscopy — ●JASMIN SÜSS¹, JOHANNES WEHNER¹, JAKUB DOSTÁL^{2,3}, TOBIAS BRIXNER^{2,3}, and VOLKER ENGEL¹ — ¹Institut für Physikalische und Theoretische Chemie, Emil-Fischer-Str. 42, 97074 Würzburg, Germany — ²Institut für Physikalische und Theoretische Chemie, Am Hubland, 97074 Würzburg, Germany — ³Center for Nanosystems Chemistry (CNC), Theodor-Boveri-Weg, 97074 Würzburg, Germany

We present a theoretical study on exciton-exciton annihilation (EEA) in a molecular dimer. This process is monitored using a fifth-order coherent two-dimensional (2D) spectroscopy as was recently proposed by Dostál *et al.* (*Nat. Commun.* **9**, 2466 (2018)). Using an electronic three-level system for each monomer, we analyze the different paths which contribute to the two-dimensional spectrum. The spectrum is determined by two entangled relaxation processes, namely the EEA and the direct relaxation of higher lying excited states. It is shown that the change of the spectrum as a function of a pulse delay can be linked directly to the presence of the EEA process.

MO 18.6 Wed 16:15 S Foyer LLM

Exciton Dynamics of Carbocyanine J-Aggregates in Polymer Films — ●STEFFEN WOLTER¹, ALEXANDER V. SOROKIN², and STEFAN LOCHBRUNNER¹ — ¹Institut für Physik, Universität Rostock, 18051 Rostock, Germany — ²Institute for Scintillation Materials of NAS of Ukraine, SSI Institute for Single Crystals of NAS of Ukraine, 60 Nauky ave., 61072 Kharkiv, Ukraine

J-aggregates are promising candidates as building blocks for future photonic applications. These supramolecular structures typically feature high quantum yields and exciton mobilities at ambient conditions, although the actual values highly depend on the local environment. J-aggregates in thin polymer films are of particular interest for applications. However, most studies deal with aggregates in solution and the behavior of the aggregates in polymers is insufficiently characterized. In this contribution, the influence of different local environments on the exciton dynamics is investigated by femtosecond pump probe spectroscopy for J-aggregates consisting of the carbocyanine dye 1,1'-disulfobutyl-3,3'-diethyl-5,5',6,6'-tetrachlorobenzimidazolylcarbo-cyanine sodium salt (TDBC). The dye forms J-aggregates in polymer films with optical properties comparable to those in water solutions, however, with a much lower fluorescence quantum yield. The goal is to understand this finding and to learn about the responsible mechanism.

MO 18.7 Wed 16:15 S Foyer LLM

THz Spectroscopy on Charge Carriers in Organic Semiconductors — ●PHILIPP KRAUSPE, JULIEN RÉHAULT, MARTINA CAUSA¹, DEMETRA TSOKKOU, and NATALIE BANERJI — Universität Bern, Freiestrasse 3, 3012 Bern

In this work we present optical pump - THz probe (OPTP) studies on organic semiconductors. [1] These semiconductors are polymer:fullerene blends which are used for organic photovoltaics. Our THz spectroscopy reveals the time evolution of charge carriers and their relative mobility on short distances. By changing the material system and selectively exciting the compounds we isolate separate pathways from photoexcitation to free carrier that transports the solar energy to the outer contacts. We present these findings in combination with transient absorption and electro differential absorption measurements on the same material systems.

Furthermore, we introduce a novel spectroscopic technique aiming at the first few picoseconds revealing the charge generation process upon photoexcitation. In this THz emission spectroscopy we generate a THz waveform within an active layer by applying a constant bias that accelerates the free charges.

[1] P. Krauspe, D. Tsokkou, M. Causa*, E. Buchaca-Domingo, Z. Fei, M. Heeney, N. Stingelin, N. Banerji: Terahertz Short-Range Mobilities in Neat and Intermixed Regions of Polymer: Fullerene Blends with Controlled Phase Morphology. *Journal of Materials Chemistry A* (2018)

MO 18.8 Wed 16:15 S Foyer LLM

Effect of External Electric Field on Charge-Pair Dynamics in Poly-[3-Hexylthiophene] (P3HT): A Femtosecond Time-Resolved Study — ●DEBKUMAR RANA, PATRICE DONFACK, VLADISLAV JOVANOVIĆ, VEIT WAGNER, and ARNULF MATERNY — Jacobs University Bremen, Department of Physics & Earth Sciences, Campus Ring 1, 28759, Bremen, Germany

Organic semiconductors have attracted considerable attention in recent years. However, a complete fundamental understanding of the relevant elementary processes is still missing. Several subtle processes such as those involving bound states (*e.g.* charge-pair states) are crucial to the overall macroscopic picture of device performance based on free charge carriers. In our contribution, we have investigated the dynamics of charge-pair states in Poly-[3-hexylthiophene] (P3HT), a promising organic semiconductor already studied by many researchers, utilizing standard and electric field-dependent transient absorption spectroscopy in order to obtain a realistic picture of the dynamics, since typical devices operate under an applied voltage in practice.

We have found that due to dissociation in the presence of external electric fields, charge-pair recombination time scales and pathways are significantly affected. Especially, our study has revealed a direct observation of different kinds of charge pairs as the result of an applied reverse bias, which we have attributed to typical polaron pairs and loosely bound polaron pairs. These charge pairs have shown completely different dynamics in our study. We will present and discuss our first experimental results.

MO 18.9 Wed 16:15 S Foyer LLM

Ultrafast Electronic Dynamics and Optical Excitation of Phonons in Hafnium Disulfide Crystals — ●SIMON UNGER¹, FRANZISKA FENNEL¹, CHRIS REHHAGEN¹, TIM VÖLZER¹, KAI ROSSNAGEL², and STEFAN LOCHBRUNNER¹ — ¹Institute for Physics, University of Rostock, Albert-Einstein-Str. 23-24, 18059 Rostock — ²Institute for Experimental and Applied Physics, University of Kiel, Leibnizstr. 19, 24118 Kiel

Transition metal dichalcogenides feature unique electronic and optical properties. Additionally, they consist of a layered structure, allowing the preparation of atomically thin crystals. Hafnium disulfide, as a representative of those materials, is considered to be a promising candidate for electronic and optoelectronic applications. To investigate the internal electronic processes and decay dynamics, static absorption and femtosecond pump-probe measurements were performed.

In the absorption spectrum, two bands are observed in the UV range. In the femtosecond pump-probe experiments, the sample is excited in the range of those bands and probed by a following white light pulse. The transient absorption signal shows a strong reduction in absorbance in the region of the original absorption, whereas at longer wavelengths a signal increase appears. This feature is an indication for a band gap renormalization induced by the population of excited charge carriers. The temporal evolution exhibits a fast sub-picosecond and a slower sub-nanosecond decay, caused by the relaxation and recombination of the charge carriers. Furthermore, the time traces show an oscillation

pattern, which can be attributed to the excitation of acoustic phonons.

MO 18.10 Wed 16:15 S Foyer LLM

Porphyrin-functionalized covalent organic cage compounds as prototypical artificial light-harvesting systems — ●LYSANNE MONIKA DIETRICH^{1,2}, MATTHIAS HENSEN¹, EVGENII TITOV¹, ROLAND MITRIC¹, FLORIAN BEUERLE², and TOBIAS BRIKNER¹ — ¹Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg — ²Institut für Organische Chemie & Zentrum für Nanosystemchemie, Universität Würzburg, Am Hubland, 97074 Würzburg

One key challenge for the future will be to learn how to construct artificial molecular devices enabling the harvesting of sunlight and their use for photosynthetic approaches. Recent studies suggested that the flexibility of the donor-acceptor linking group of artificial photosynthetic materials is an important parameter for optimizing their performance [1]. In order to improve the understanding of photoinduced electron transfer processes characteristic of photosynthesis, we designed a novel porphyrin-containing covalent organic cage compound that can serve as an efficient host for [60]fullerene. Upon photoexcitation of the porphyrin donor moiety, an electron transfer to the encapsulated [60]fullerene is triggered presumably on the ultrafast timescale. Here we report on investigations on electron transfer processes of these supramolecular porphyrin fullerene hybrid systems by means of femtosecond transient absorption spectroscopy and quantum chemical calculations.

[1] C. A. Rozzi et. al., *Nat. Commun.* 4, 1602 (2013).

MO 18.11 Wed 16:15 S Foyer LLM

Transient Absorption Spectroscopy of Photo-induced Guest Uptake and Release by a Photochromic Coordination Cage — ●KEVIN ARTMANN¹, RUJIN LI², DOMINIK WELZEL¹, GUIDO H. CLEVER², and PATRICK NUERNBERGER¹ — ¹Physikalische Chemie II, Ruhr-Universität Bochum, 44780 Bochum — ²Anorganische Chemie, Technische Universität Dortmund, 44227 Dortmund

Encapsulation of guest compounds by molecular cages are a promising tool in a variety of applications. It can be used to protect, to transport, or to influence the reactivity of guest molecules, but also *vice versa* the guest may modify the properties of the host. Recently, Han *et al.* demonstrated that it is possible to trigger the reversible guest encapsulation with light by using cage systems composed of photo-switchable dithienylethene ligands [1].

In this study we investigate the influence of a guest compound on the ultrafast photodynamics of these cages. We demonstrate that the dynamics of the single ligand and of the cage in solution are similar to those of a closely related derivative examined by Ern *et al.* [2]. Furthermore, we show that the photodynamics of the cage with ring-closed ligands do not change after addition of the guest. In contrast, encapsulation of the guest in cages with ring-open ligands reduces the efficiency of the ring-closing reaction and gives rise to the population of another intermediate state.

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

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

MO 18.12 Wed 16:15 S Foyer LLM

Excited State Dynamics of the Amino Acid Tryptophan — ●PASCAL ENGL, JANINA LEBENDIG-KUHLE, and ANDREA LÜBCKE — Max-Born-Institut für Nichtlineare Optik und Kurzzeitspektroskopie, Berlin

The amino acid tryptophan is known to be involved in ultra-fast processes like energy and electron transfers in proteins. We investigate the excited state dynamics of tryptophan in solution and its chromophore indole in the gas phase by utilizing pump-probe time-resolved photoelectron spectroscopy (TRPES). This method allows us to follow photoreactions in both energy and time by mapping the molecule's excited state dynamics onto the continuum. As pump and probe pulses we use fs UV-laser pulses with wavelengths of 200 nm and 266 nm. For the measurements in aqueous solution we employ the liquid microjet technique. We will describe our experimental setup, present our results and discuss the effects of the environment on the excited state dynamics.

MO 18.13 Wed 16:15 S Foyer LLM

Quick Photoshoot: time-resolved imaging of the azobenzene isomerization with ultra-fast electron diffraction — ●MARIO NIEBUHR¹, KEITH JOBE², RENKAI LI², J. PEDRO F. NUNES⁴, XIAOZHE SHEN², STEPHEN WEATHERSBY², THOMAS J. A. WOLF³,

CHARLES YONEDA², JIE YANG^{2,3}, MARTIN CENTURION⁴, XIJIE WANG², and MARKUS GÜHR¹ — ¹Institute for Physics and Astronomy, Uni Potsdam, Germany — ²SLAC National Accelerator Laboratory, USA — ³PULSE Institute, SLAC National Accelerator Laboratory, USA — ⁴Department of Physics & Astronomy, University of Nebraska-Lincoln, USA

The processes involved in the trans-cis isomerization of azobenzene are still actively discussed. One issue in question are different proposed relaxation pathways after Vis or UV excitation, resulting in distinct intermediate geometries. While calculations generally suggest the so called inversion pathway, to our knowledge no direct observation has been performed confirming one or the other.

Photon pump electron probe diffraction experiments on isolated molecules in the gas phase promise to allow just that. New ultrafast electron diffraction setups with MeV beams offer a new approach to that question [1] mitigating the disadvantages of current keV systems (velocity mismatch, electron beam divergence) and allowing for sub-100 fs time resolution to observe the azobenzene reconfiguration during the trans-cis isomerization. We will show results from our first run with the UED group at SLAC and discuss planned improvements.

[1] Weathersby et al., Rev. Sci. Instrum. **86**, 073702 (2015)

MO 18.14 Wed 16:15 S Foyer LLM

Charge transfer in mixed valence states: Relaxation dynamics and transient absorption spectroscopy — ●FABIAN GLAAB¹, JOHANNES WEHNER¹, CHRISTOPH LAMBERT², and VOLKER ENGEL¹ — ¹Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Emil-Fischer-Str. 42, 97074 Würzburg, Germany — ²Institut für Organische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

Quantum dynamical model calculations are performed on the laser-induced dynamics of mixed valence systems. The simultaneously occurring processes of non-adiabatic population transfer and relaxation are studied in detail. Transient absorption traces, as recently recorded in our laboratory [1], are simulated, and the features of the spectra are related to the dynamics. The agreement with experiment hint at the fact that the employed one-dimensional model catches the essentials of the photochemistry of the mixed valence systems under consideration.

[1] C. Lambert, M. Moos, A. Schmiedel, M. Holzappel, J. Schäfer, M. Kess, V. Engel, V., Phys. Chem. Chem. Phys. **18**, 19405-19411 (2016).

MO 18.15 Wed 16:15 S Foyer LLM

Multidimensional electronic spectroscopy of a molecular beam with mass-resolved ion detection — ●HANS-PETER SOLOWAN, TRISTAN FORD, SEBASTIAN ROEDING, and TOBIAS BRIXNER — Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

We report on the progress with 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 [1].

Using a pulse shaper based on an acousto-optic programmable dispersive filter and rapid scanning [2] we focus a train of four collinear pulses in the visible regime into an interaction region with a molecular beam. Via phase cycling [3] the signals of the time-of-flight mass spectrometer can be disentangled to extract the different contributions, like the photon-echo response. We have recently installed a preparation chamber for a supersonic molecular beam with argon as a seed gas. This allows us to investigate not only gaseous samples but also liquid and solid ones that are evaporated by an oven.

[1] S. Roeding and T. Brixner, Nat. Commun. **9**, 2519 (2018)

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

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

MO 18.16 Wed 16:15 S Foyer LLM

Ultrafast 2D-Vis spectroelectrochemistry — ●JULIA HEITMÜLLER, KLAUS ECKSTEIN, PASCAL KUNKEL, TOBIAS BRIXNER, and TOBIAS HERTEL — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

Coherent 2D spectroscopy is a well established method to investigate dynamic processes with femtosecond time resolution and to observe

couplings between different energetic states. Electrochemistry is used to generate different oxidized and reduced molecular species in solution. Our goal is the combination of these two techniques leading to coherent 2D spectroelectrochemistry. For the infrared regime different spectroelectrochemical cells were described and used for 2D measurements in the literature [1,2]. We developed a prototype for the visible regime to investigate UV/Vis-induced photophysics or photochemical reactions depending on oxidation state. We verified that our design works, by using redox standards and laser dyes. First time-resolved measurements were performed by integrating the cell in transient absorption experiments. In the next step we will approach 2D spectroscopy and observe molecules in different redox states, that are generated *in situ* without adding oxidizing or reducing agents.

[1] Y. El Khoury, et al., Rev. Sci. Instrum. **86**, 083102 (2015)

[2] D. Lotti, et al., J. Phys. Chem. C, **120**, 2883 (2016)

MO 18.17 Wed 16:15 S Foyer LLM

Ultrafast Photoelectron Circular Dichroism Changes in 1-Iodo-2-methylbutane — ●V. MUSIC^{1,2}, F. ALLUM⁴, S. BARI³, T. M. BAUMANN¹, R. BOLL¹, S. DOERNER³, A. EHRESMANN², B. ERK³, P. GRZYCHTOL¹, G. HARTMANN², A. KNIE², M. LARSSON⁷, J. LEE⁴, B. MANSCHWETUS³, L. MARDER², R. MASON⁴, M. MEYER¹, H. OTTO², D. ROLLES⁵, P. SCHMIDT², K. SCHUBERT³, L. SCHWOB³, R. WAGNER¹, V. ZHAUNERCHYK⁶, and M. ILCHEN^{1,2} — ¹European XFEL GmbH, Schenefeld, Germany — ²University of Kassel, Germany — ³DESY, Hamburg, Germany — ⁴University of Oxford, UK — ⁵Kansas State University, Manhattan, USA — ⁶University of Gothenburg, Sweden — ⁷AlbaNova University Center, Stockholm, Sweden.

Highly intense circularly polarized XUV free-electron laser pulses were used to observe the time-resolved photoelectron circular dichroism (TR-PECD) of a prototypical chiral molecule as 1-Iodo-2-methylbutane ($C_5H_{11}I$) during laser induced fragmentation. The presented experiment was performed at the BL1 CAMP endstation at FLASH1 in Hamburg. With a two-sided velocity map imaging spectrometer, electron-ion correlations were obtained and the time-resolved ejection of ionic and neutral atomic iodine was observed. These fragments serve as observer site to monitor the evolving chirality of the molecule. For probing the different fragmentation channels of the chiral molecule (R-enantiomer, S-enantiomer and the racemic mixture), two different photon energies, i.e. 63 eV (for neutral iodine) and 75 eV (for singly charged iodine), were used.

MO 18.18 Wed 16:15 S Foyer LLM

Theoretical interpretation of angular-resolved photoelectron pump-probe spectroscopy — ●ANDY KAISER, SERGEY BOKAREV, and OLIVER KÜHN — Institute of Physics, Rostock, Germany

Photoelectron spectroscopy is a powerful probe of the electronic structure of atoms and molecules. Orbital structure, energy levels and non-adiabatic dynamics can be analyzed within pump-probe experiments. Varying the time delay between the pulses gives information about wave packet dynamics and potential energy surfaces. This knowledge allows to optimize chemical processes and learn about spin crossover phenomena. In this work randomly oriented transition metal complexes were studied theoretically in the solution phase. First, molecules are preselected by a short pump-pulse. After a short time delay, which lies in fs range such that translational and rotational degrees of freedom can be considered as frozen, the sample interacts with the probe pulse, ejecting a photoelectron, which is then resolved angularly giving information about the electronic structure. The working expression in this simulation is the photoelectron matrix element formulated in the Dyson orbital formalism and the outgoing photoelectron described by Coulomb waves. To obtain accurate energies of both, the system and the photoelectron, optimally-tuned, range-separated density functionals were used within TDDFT.

MO 18.19 Wed 16:15 S Foyer LLM

Pulse Length Dependence of Photoelectron Circular Dichroism — ROXANA SAVULEA, ●SIMON T. RANECKY, CONSTANTIN WITTE, ALEXANDER KASTNER, TOM RING, HAN-GYEOL LEE, SUDHEENDRAN VASUDEVAN, HENDRIKE BRAUN, DANIEL REICH, ARNE SENFTLEBEN, and THOMAS BAUMERT — Universität Kassel, Institut für Physik und CINSaT, D-34132 Kassel, Germany

The asymmetry of photoelectron angular distributions from randomly oriented enantiomers of chiral molecules in the ionization with circularly polarized light arises in forward/backward direction with respect to the light propagation direction. This effect is known as photoelec-

tron circular dichroism (PECD) and has been investigated by single-photon [1] as well as resonance-enhanced multi-photon ionization using a femtosecond laser [2, 3]. In that case, ionization occurs out a frozen nuclear configuration. For longer pulses, additional dynamics like internal conversion, intra-molecular vibrational energy redistribution, vibrations or rotation of the molecules come into play.

Here we present a coherent pulse length study to investigate PECD ranging from the femtosecond to the nanosecond regime. To that end, we employ a femtosecond laser with variable pulse duration and a nanosecond dye laser. When using the latter, the lifetime of the intermediate states is much shorter than the pulse duration of the laser.

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

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

[3] A. Kastner et al., *J. Chem. Phys.* 147, 013926, (2017)

MO 18.20 Wed 16:15 S Foyer LLM

Role of coherence for photoelectron circular dichroism after multi-photon excitation in randomly oriented chiral molecules — ●ALEXANDER BLECH¹, R. ESTEBAN GOETZ¹, TIMUR A. ISAEV², BEHNAM NIKOBAKH², ROBERT BERGER², and CHRIS-

TANE P. KOCH¹ — ¹Universität Kassel, Deutschland — ²Philipps-Universität Marburg, Deutschland

Photoelectron circular dichroism (PECD) refers to the forward/backward asymmetry in the photoelectron angular distribution with respect to the propagation axis of circularly polarized light. Our existing model for PECD in resonantly enhanced multi-photon ionisation of randomly oriented chiral molecules is based on perturbation theory for the light-matter interaction and on ab initio calculations for the multi-photon absorption, giving semi-quantitative agreement with experimental data for fenchone and camphor and enabling application of coherent control.

Here we want to extend this model to explicitly take into account the chirality of the photoelectron continuum and the coherence between non-resonant multi-photon excitation and one-photon ionisation by standard quantum beat spectroscopy of electronic superposition states in a pump-probe scheme. Our extended model will allow us to distinguish the contributions of intermediate and final states to PECD and to refine our quantum optimal control approach in order to determine the ultimate strength of the chiral response.

MO 19: Cluster III (joint session MO/A)

Time: Thursday 10:30–12:30

Location: S HS 001 Biologie

Invited Talk

MO 19.1 Thu 10:30 S HS 001 Biologie

Optical spectroscopy of small metal clusters: a deeper look at Au₄⁺ — ●MARKO FÖRSTEL, WOLFGANG SCHEWE, and OTTO DOPFER — TU Berlin, IOAP, Hardenbergstr. 36, 10623 Berlin

The catalytic properties of small metal clusters strongly depend on local structure. This is especially the case for very small clusters, where every new atom changes the physical and thus catalytic properties tremendously. For example, gold clusters show catalytic properties at sizes down to three atoms!

With a new setup we were able to measure the optical absorption spectrum of such small gold clusters in hitherto unavailable quality.^[1] These spectra allow for the first time to directly access the structure of the ground and excited state via comparison of the measured vibrational frequencies and Franck-Condon progressions to those from calculated structures. Surprisingly, we find that the optical spectrum cannot be explained by assuming that it stems solely from the rhombic ground state structure of Au₄⁺.^[2]

[1] M. Förstel, B. K. A. Jaeger, W. Schewe, P. H. A. Sporkhorst, O. Dopfer, Improved tandem mass spectrometer coupled to a laser vaporization cluster ion source *Rev. Sci. Instr.* 2017, 88, 123110.

[2] M. Förstel, W. Schewe, O. Dopfer, Optical spectroscopy of the Au₄⁺ cluster: Resolved vibronic structure indicates an unexpected isomer, *submitted*.

MO 19.2 Thu 11:00 S HS 001 Biologie

Activation of Methane by Free Gold Clusters: Ion-Trap Kinetics, IR-Spectroscopy, and Ab Initio Theory — ●THORSTEN BERNHARDT¹, SANDRA LANG¹, JOOST BAKKER², ROBERT BARNETT³, and UZI LANDMAN³ — ¹Institute of Surface Chemistry and Catalysis, University of Ulm, 89069 Ulm, Germany — ²Institute for Molecules and Materials, FELIX Laboratory, 6525 ED Nijmegen, The Netherlands — ³School of Physics, Georgia Institute of Technology, Atlanta, Georgia 30332-0430, USA

Amongst all the metals gold exhibits the least inclination to undergo chemical reactions with other elements. It is therefore even more surprising that few nanometer sized gold particles and gold clusters consisting of very few atoms display excellent catalytic properties. In order to demonstrate the ability of small gold clusters to activate methane, we previously performed gas phase reaction kinetics experiments in an octopole ion trap. These experimental studies revealed the particular catalytic properties of the gold dimer to activate methane and to convert two methane molecules to ethylene at thermal reaction conditions. These experiments have now been complemented by infrared multi photon dissociation experiments employing the free electron laser FELICE at the University of Nijmegen. These spectroscopy investigations demonstrated that the interaction of methane with small gold cluster cations leads to selective C-H-bond dissociation and the formation of hydrido-methyl complexes.

MO 19.3 Thu 11:15 S HS 001 Biologie

Interspecies energy transfer in heterogeneous Ar₂-N₂ clusters quenching predissociation — ●HUDA OTTO, DANA BLOSS, ANDREAS HANS, XAVER HOLZAPFEL, CATMARNA KÜSTNER-WETEKAM, CHRISTIAN OZGA, PHILIPP SCHMIDT, ARNO EHRESMANN, and ANDRÉ KNIE — Institut für Physik und Center for Interdisciplinary Nanostructure Science and Technology (CINSaT), Universität Kassel, Heinrich-Plett-Straße 40, 34132 Kassel, Germany

Loosely bound systems, like Ar₂, are of technical and biological interest. For example, the Ar dimer (Ar₂) is used as a medium in excimer lamps, and decay processes in such noble gas dimers are showcase examples to explain radiation damage in organic tissues. Ar₂ consists of two *van-der-Waals bound* Ar atoms. This binding type affects the energy transfer between van-der-Waals bound atoms, called clusters. Doping an Ar cluster with a molecule, like N₂, allows to investigate the effect of molecular vibrations on energy transfers in a loosely bound environment. Here, different vibronic states of N₂ in an Ar₂-N₂ cluster were addressed. In gaseous N₂ the resonant excitation of these vibronic states lead to non-radiative predissociation, whereas if the N₂ is van-der-Waals bound on an Ar cluster, the absorbed energy is redistributed within the cluster, resulting in photon emission from perturbed Ar dimers. Thus, an interspecies energy transfer from a N₂ molecule to an Ar dimer must occur. During the talk evidences for the interspecies energy transfer in heterogeneous Ar₂-N₂ clusters will be discussed further.

MO 19.4 Thu 11:30 S HS 001 Biologie

Electron and photon interactions with size-selected lead clusters — STEFFI BANDELOW, ●ALEXANDER JANKOWSKI, STEPHAN KÖNIG, GERRIT MARX, LUTZ SCHWEIKHARD, and MARKUS WOLFRAM — Institute for Physics, University of Greifswald, Germany

At the ClusterTrap-setup [1], the dissociation pattern of photoexcited lead cluster ions has been of interest in recent studies [2,3]. It was shown that lead transitions from a metallic [4] to a non-metallic fragmentation behavior [2] when approaching smaller cluster sizes. In further investigations, size-selected trapped negatively charged lead clusters are exposed to an electron beam. This leads to electron attachment [5,6] as well as collision-induced dissociation [6]. The resulting product ions reveal first hints of fission processes, where doubly negatively charged clusters break up into two singly charged fragments. The most prominent fragments observed are Pb₁₀¹⁻, and Pb_{n-10}¹⁻, where *n* is the precursor cluster size. This interpretation is confirmed by photodissociation studies of size- and charge-state selected dianionic lead clusters [7].

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

[2] S. König *et al.*, *J. Phys. Chem. C* 121 (2017) 10858.

[3] M. Wolfram *et al.*, *J. Phys. B: At. Mol. Opt.* 51 (2018) 044005.

[4] P.J. Brucat *et al.*, *J. Chem. Phys.* 84 (1986) 3078.

[5] A. Herlert *et al.*, *Phys. Scripta* T80 (1999) 200.

- [6] S. König *et al.*, *Int. J. Mass Spectrom.* 421 (2017) 129.
 [7] S. König *et al.*, *Phys. Rev. Lett.* 120 (2018) 163001.

MO 19.5 Thu 11:45 S HS 001 Biologie

Photophysics investigation of pyrrole and pyrrole-water₁ clusters — ●MELBY JOHNY¹, SEBASTIAN TRIPPEL^{1,2}, and JOCHEN KÜPPER^{1,2,3} — ¹Center for Free-Electron Laser Science, DESY, Hamburg — ²The Hamburg Center for Ultrafast Imaging, Universität Hamburg, Hamburg — ³Department of Physics, Universität Hamburg, Hamburg

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.

Here, we show the investigation of the photophysics of pyrrole and the single hydrogen bonded pyrrole-water₁ clusters via site-specific x-ray ionisation and strong field ionisation by intense near-infrared laser pulses. The photo-fragmentation owing to core-shell ionisation at nitrogen(N 1s) were analyzed by means of photoelectron photoion-photoion coincidence(PEPIPICO) imaging. A 3D-imaging detector, Timepix3 was used for coincidence detection of strong field ionisation of pyrrole and pyrrole-water₁. For pyrrole-water₁ clusters, we observed proton or hydrogen atom transfer from pyrrole moiety to the hydrogen bonded water molecule and the fragmentation dynamics is significantly different from bare pyrrole.

MO 19.6 Thu 12:00 S HS 001 Biologie

Superelectrophilic Behaviour of closo-Dodecaborate Monoanions — KNUT R. ASMIS¹, MARTIN MAYER¹, JONAS WARNEKE², and ●MAX GRELLMANN¹ — ¹Wilhelm-Ostwald-Institut für Physikalische und Theoretische Chemie, Universität Leipzig, Linnestr. 2, 04103 Leipzig (Germany) — ²Department of Chemistry, Purdue University, West Lafayette, IN 47907 (USA)

Bond formation with an electron-rich system, known as electrophilicity, is commonly observed in electron-deficient molecules. Binding noble gases at room temperature was a marking property predominantly of strong, dicationic systems, therefore termed as *superelec-

trophiles*. Gas-phase skimmer collision induced dissociation (sCID) lead to the formation of closo-dodecaborate monoanions [B₁₂X₁₁]⁻, showing a high reactivity towards electron-rich systems for instance dinitrogen, dioxygen and noble gases (Ngs). In particular, the clusters [B₁₂X₁₁]⁻ (X = Cl, CN) have been observed to form spontaneously B-Ng bonds with a substantial degree of covalent interaction, thus showing a superelectrophilic behaviour despite being negatively charged. A significant blue shift of the CO stretching mode when bound with its carbon tail to a closo-dodecaborate monoanion, observed by using infrared photodissociation (IRPD) spectroscopy, verified the suspected electron-deficiency at the binding site of the cluster. Quantum chemical calculations revealed that the anions unite several molecular properties, which lead to a dipole discriminating chemistry, facilitating the addition of Ngs. On this account, small dipole moments of alkanes could be a promising property to introduce the anions into C-H-bond activation.

MO 19.7 Thu 12:15 S HS 001 Biologie

Photofragmentation of small bismuth clusters — ●PAUL FISCHER, GERRIT MARX, and LUTZ SCHWEIKHARD — Institut für Physik, Universität Greifswald, 17489 Greifswald, Germany

Bismuth clusters Bi_n^{+/-} in the size range n = 2 to 19 have been produced by laser ablation and stored in an electrostatic ion beam trap (EIBT) [1,2]. The trap allows the retention of size-selected ions and their separation from contaminant ions with high resolving powers [3].

Photofragmentation has been performed by use of nanosecond laser pulses (λ = 532nm). Product patterns include multiple cluster sizes, depending on the selected precursor. To further investigate the fragmentation pathways of the clusters, parameters such as the laser-pulse energy and timing have been varied. In many cases, the preliminary data evaluation suggests pathway competition and only a few sequential decays. The size of the primary neutral fragment being evaporated shifts with increasing precursor cluster size.

- [1] H. Wollnik *et al.*, *J. Mass Spectrom.* Ion Processes 96(3):267-274(1990)

- [2] D. Zajfman *et al.*, *Phys. Rev. A* 55:R1577-R1580(1997)

- [3] P. Fischer *et al.*, *Rev. Sci. Instrum.* 89:015114(2018)

MO 20: Atomic Physics, Molecular Physics, and Quantum Optics with X-ray FELs (joint session MO/A)

Time: Thursday 10:30–12:30

Location: S HS 002 Biologie

MO 20.1 Thu 10:30 S HS 002 Biologie

Nanodroplet production and characterization for single particle X-ray diffractive imaging — ●AMINE GOURRAM¹, ARMANDO ESTILLORE¹, DANIEL HORKE^{1,3}, and JOCHEN KÜPPER^{1,2,3} — ¹Center for Free-Electron Laser Science, DESY, Hamburg, Germany — ²Department of Physics, University of Hamburg, Hamburg, Germany — ³The Hamburg Center for Ultrafast Imaging, University of 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. Express* 24, 6507-6521 (2016)

MO 20.2 Thu 10:45 S HS 002 Biologie

3D sensitive diffractive imaging of metal cluster shape transitions — ●J. JORDAN¹, S. DOLD², I. BARKE³, P. BEHRENS¹, N. BERNHARDT¹, J. CORREA⁴, S. DÜSTERER⁴, B. ERK⁴, L. HECHT¹, A. HEILRATH¹, H. HARTMANN³, R. IRSIG³, N. IWE³, B. KRUSE³, B. LANGBEHN¹, B. MANSCHWETUS⁴, F. MARTINEZ³, K. OLDENBURG³, C. PASSOW⁴, C. PELTZ³, F. SEEL¹, R. TANYAG⁵, R. TREUSCH⁴, A. ULMER¹, S. WALZ¹, K.-H. MEIWES-BROER³, T. FENNEL^{3,5}, B. V. ISSENDORFF², T. MÖLLER¹, and D. RUPP^{1,5} — ¹TU Berlin — ²Univ.

Freiburg — ³Univ.Rostock — ⁴FLASH@DESY — ⁵MBI Berlin

With their ability to deliver ultra-short X-ray pulses of high brilliance, free-electron lasers (FELs) have opened up new possibilities for natural sciences. In cluster physics, FELs have been used to investigate fundamental light-matter interactions and create scattering images of single clusters in free flight for structure determination. In particular, gas phase metal clusters exhibit a large variety of shapes that are very sensitive to the growth conditions. Their shape can be altered by soft heating, leading to a reordering of the crystal lattice or melting of the surface. In order to image these changes and record their intrinsic timescale, we performed a pump-probe experiment at the FLASH FEL in Hamburg. Silver clusters were produced using a magnetron sputter source and subsequently heated with a picosecond-long, weak optical laser pulse. The temporal evolution of the shapes after excitation was traced by recording wide-angle scattering images that enable a 3D sensitive shape retrieval.

MO 20.3 Thu 11:00 S HS 002 Biologie

Neural Networks for Reconstruction of Nanoclusters from Soft X-Ray Scattering Images — ●THOMAS STIELOW, ROBIN SCHMIDT, THOMAS FENNEL, and STEFAN SCHEEL — Institut für Physik, Universität Rostock, Albert-Einstein-Straße 23, 18059 Rostock

Single-shot diffraction imaging by soft X-ray laser pulses is a valuable tool for structural analyses of unsupported and short-lived nanosystems, although inversion of the scattering patterns still prove challenging. Deep learning, on the other hand, is widely used in data sciences for the extraction of information from images and sees more and more application in various sciences. We demonstrate how neural networks can be utilized for full reconstructions of nanoclusters from single-shot wide angle scattering images. Our networks are trained

solely on existing physical theories and can be applied to real-world experimental data without limitation to a specific setup due to its robustness. With deep learning, high quality real time evaluation for the next generation FEL systems can finally be implemented.

MO 20.4 Thu 11:15 S HS 002 Biologie

Controlling nanoparticles with external fields — ●JANNIK LÜBKE¹, SALAH AWEL^{1,4}, ARMANDO ESTILLORE¹, NILS ROTH^{1,2}, AMIT SAMANTA¹, LENA WORBS¹, DANIEL HORKE^{1,4}, and JOCHEN KÜPPER^{1,2,3,4} — ¹Center for Free-Electron Laser Science (CFEL), Deutsches Elektronen-Synchrotron (DESY), Hamburg, Germany — ²Department of Physics, Universität Hamburg, Germany — ³Department of Chemistry, Universität Hamburg, Germany — ⁴The Hamburg Center for Ultrafast Imaging (CUI), Universität Hamburg,

In single-particle coherent x-ray diffraction experiments, diffraction patterns are recorded from individual sample particles. To overcome the inherently small signal-to-noise ratio, large numbers of identical particles need to be controlled and guided subsequently into the small focus of free-electron lasers (FELs). We establish particle control for example *via* electrostatic deflection or optical guiding in tractor beams [1], ultimately aiming at delivering one nanoparticle at a time into successive FEL shots.

[1] Eckerskorn et al., *Proc. SPIE* **9548**, 95480H1-95480H12, 2015

MO 20.5 Thu 11:30 S HS 002 Biologie

Detecting ultrafast hole dynamics in water using x-ray transient absorption — ●CAROLINE ARNOLD^{1,2,4}, LUDGER INHETER¹, RALPH WELSCH^{1,4}, LINDA YOUNG³, and ROBIN SANTRA^{1,2,4} — ¹Deutsches Elektronensynchrotron DESY, Hamburg — ²Universität Hamburg — ³Argonne National Laboratory, USA — ⁴Centre for Ultrafast Imaging, Hamburg

The dynamics that unfold in aqueous solutions on a molecular time scale are of direct relevance to biological and chemical processes. For example, radiation damage in biological tissues is caused by the photoionization of liquid water. The early steps of radiation damage can be understood by following the electron-hole pair dynamics with femtosecond time-resolution. While the hydrated electron has been addressed in experiments, the dynamics of the residual cation remains elusive. Today's XFEL sources allow to detect the hole by resonant x-ray absorption spectroscopy at the oxygen K-edge with femtosecond time resolution.

We present a theoretical, *ab initio* description of the hole dynamics in ionized water and the resulting x-ray absorption spectra. To this end, we consider excited-state molecular dynamics in liquid water following the removal of an electron from the valence band in a quantum-classical, QM/MM scheme including non-adiabatic transitions. We present first results on time-resolved x-ray absorption spectra in the first 100 femtoseconds following photoionization and discuss their use as a probe for hole dynamics.

MO 20.6 Thu 11:45 S HS 002 Biologie

X-ray emission spectroscopy using dispersive spectrometers at Synchrotron and X-ray FEL facilities — ●FLORIAN OTTE^{1,2}, CHRISTIAN BRESSLER², and METIN TOLAN¹ — ¹Technische Universität Dortmund, Emil-Figge-Straße 50, 44227 Dortmund, Deutschland — ²European XFEL GmbH, Holzkoppel 4, 22869 Schenefeld, Deutschland

Crystal spectrometers which enable the energy dispersive detection of X-ray fluorescence during irradiation with intense X-rays have found widespread distribution among X-ray facilities worldwide. Different designs and types exist, but all of them appeal through their ability to track electronic and magnetic properties of samples via characteristic features in X-ray emission signals during the experiment. Which elec-

tronic and magnetic properties are accessible specifically, is case and spectrometer dependent. We report on the use of an energy-dispersive von Hamos type spectrometer, which is being used at the FXE instrument at European XFEL GmbH on a regular basis in combination with additional complimentary experimental techniques such as X-ray diffraction for detection of K-edge emission lines on transition metal complexes. A smaller and highly mobile version of this spectrometer type has been successfully used at different beamlines (e.g. P01 at Petra III in Hamburg, B19 at DELTA in Dortmund). The highly flexible nature of this spectrometer type is rationalized with experimental results on transition metal complexes. Advantages and disadvantages in comparison with other available spectrometer types are discussed, with special consideration of applications at modern FELs.

MO 20.7 Thu 12:00 S HS 002 Biologie

Giant Enhancement of Molecular Ionization at High X-ray Intensity — ●LUDGER INHETER¹, YAJIANG HAO², SANG-KIL SON¹, and ROBIN SANTRA^{1,3} — ¹Center for Free-Electron Laser Science, DESY, Hamburg — ²Department of Physics, University of Science and Technology Beijing — ³Department of Physics, Universität Hamburg

The ultraintense and ultrashort x-ray pulses provided by X-ray Free-Electron Lasers (XFELs) sequentially ionize molecular samples many times. We have developed an *ab-initio* electronic structure toolkit, XMOLECULE[1,2], that models this multiple ionization dynamics. Our calculations show that the rearrangement of charges between different parts of a molecule plays an important role for the ion yield distribution. In this context, we have recently discovered that under intense x-ray radiation the total charge yield of a molecule is enhanced compared to independent atoms[2,3].

We report here on new theoretical results for iodobenzene (C₆H₅I) that show an even stronger ionization enhancement than previously observed for iodomethane (CH₃I)[3]. This finding emphasizes the relevance of the charge-rearrangement-enhanced X-ray ionization of molecules (CREXIM) for the radiation damage in experiments with tightly focused XFEL beams.

[1] Struct. Dyn. **2**, 041707 (2015). [2] Phys. Rev. A **94**, 023422 (2016) [3] Nature **546**, 129-132 (2017)

MO 20.8 Thu 12:15 S HS 002 Biologie

The Auger effect in dispersing and absorbing environments — ●JANINE FRANZ¹, STEFAN YOSHI BUHMANN^{1,2}, and ROBERT BENNETT^{1,2} — ¹Institute of Physics, University of Freiburg, Germany — ²Freiburg Institute for Advanced Studies (FRIAS), Germany

The Auger effect is the radiationless decay of an inner-shell ionised atom. In this process, the atom relaxes by filling the inner vacancy with an outer shell electron, but instead of releasing the excess energy in form of a photon (spontaneous decay) the energy is reabsorbed by another electron belonging to the same atom. This effect finds many applications: for example in Auger electron spectroscopy, it is used to study material properties of surfaces.

It is well established that dielectric environments can have a significant impact on spontaneous decay (Purcell effect) [1] as well as interatomic energy transfer rates [2]. We present a general expression for the intra-atomic Auger process in the presence of dielectric environments that can be used both as a new starting point for *ab initio* quantum chemistry, or within the quantum-optical formalism of macroscopic quantum electrodynamics in order to circumvent complex numerics. Within our description, the decay rate can be given in analytical form for some simple environments. We compare Auger decay with a competing process known as interatomic Coulombic decay, focussing on their behaviour in the presence of surfaces.

[1] E. M. Purcell, Proc. Am. Phys. Soc. **69**, 674 (1946).

[2] J. L. Hemmerich, R. Bennett and S. Y. Buhmann, Nature Commun. **9**, 2934 (2018).

MO 21: Coupled Systems

Time: Thursday 14:00–16:00

Location: S HS 001 Biologie

Invited Talk

MO 21.1 Thu 14:00 S HS 001 Biologie

Influence of Local and External Electric Fields on the Ultrafast Dynamics of Charge Pairs Photo-Generated in Poly-[3-Hexylthiophene] (P3HT) — DEBKUMAR RANA, TAHIRZEB KHAN, PATRICE DONFACK, VLADISLAV JOVANOVIĆ, VEIT WAGNER, and ●ARNULF MATERNY — Jacobs University Bremen, Department of

Physics & Earth Sciences, Campus Ring 1, 28759, Bremen, Germany
Organic semiconductors have attracted considerable attention in recent years due to their various advantages. However, both stability and efficiency of organic electronic devices still have to be improved. For this purpose, a detailed understanding of basic processes is of great

importance. While the investigation of neat semiconductor material will always be the starting point, in the end, more realistic scenarios have to be considered as well. On this account, we have studied the dynamics of charge-pair states in poly-[3-hexylthiophene] (P3HT), a promising organic semiconductor *e.g.* for building solar cells, utilizing femtosecond time-resolved transient absorption spectroscopy influenced by internal and external electric fields. Using sub-diffraction-limited microscopy, we were able to detect the dynamics at the interface between P3HT and a gold electrode. Additionally, in P3HT-only diodes, we have applied external fields in reverse and forward bias. In all cases, we found changes in the observed polaron-pair dynamics compared to the neat-P3HT sample without internal and external electric fields. In our presentation, we will give an overview about the experimental techniques applied as well as the interesting results we have obtained.

MO 21.2 Thu 14:30 S HS 001 Biologie

Exciton migration in multi-stranded J-type aggregates — ●CHRIS REHHAGEN¹, FRANZISKA FENNEL¹, STEFANIE HERBST², FRANK WÜRTHNER², and STEFAN LOCHBRUNNER¹ — ¹Institut für Physik, Universität Rostock, Albert-Einstein-Str. 23, 18059 Rostock — ²Institut für Organische Chemie & Center for Nanosystems Chemistry, Universität Würzburg, Am Hubland, 97074 Würzburg

Understanding the transport mechanisms of electronic excitations in coupled molecular systems is the basis for their application in light harvesting and opto-electronic devices. The exciton transfer properties depend pivotal on the supramolecular structure. Herbst et. al. reported recently a series of perylene bisimides dyes self-assembling into multi-stranded (two to four) J-type aggregates [1]. These aggregates are an ideal model system to study the impact of structural modifications onto the exciton transfer distances. We determine the exciton mobility for these aggregates by analyzing the dynamics associated with exciton-exciton annihilation [2]. Therefore energy dependent pump-probe spectroscopy is applied and a one-dimensional diffusion model is fitted to the obtained data. We compare the exciton mobilities of the different samples with respect to their supramolecular structure. Our results imply that such PBI-aggregates and their molecular engineering are promising for further applications in photonics.

[1] Herbst et. al., Nat. Commun., 9 (2018), 2646.

[2] Wolter et. al., J. Phys. B: At. Mol. Opt. Phys. 50 (2017), 184005.

MO 21.3 Thu 14:45 S HS 001 Biologie

Franck Condon spectra of the 3-tolunitrile dimer — ●CHRISTIAN HENRICHs and MICHAEL SCHMITT — Institute for Physical Chemistry I, Heinrich-Heine-University, Düsseldorf

The 3-tolunitrile (3-TN) dimer is an example for the class of centrosymmetric homodimers. The investigation of the structure of dimers has been of certain interest with respect to excitonic effects. Therefore, we have to face the question if the homodimer forms J-aggregates or H-aggregates. But not only the structure, but also the question of electronic excitation of the two equivalent chromophores might be interesting. The question is, if the electronic excitation is localized on one of the chromophores, or delocalized over the both. To address these two problems we performed Franck-Condon Fits of the fluorescence emission spectra of the 3-TN dimer and determined the change of the geometry upon electronic excitation via a Franck-Condon fit.

MO 21.4 Thu 15:00 S HS 001 Biologie

Spectroscopic observation of protein influence on charge transfer dynamics in individual YM210W reaction centers of purple bacteria — ●PAVEL MALÝ^{1,2,4}, MICHAEL R. JONES³, TOMÁŠ MANČAL¹, and RIENK VAN GRONDELLE² — ¹Charles University, Prague, Czech Republic — ²Vrije Universiteit Amsterdam, The Netherlands — ³University of Bristol, United Kingdom — ⁴present address: University of Würzburg, Germany

In photosynthetic reaction centers (RCs) the energy from sunlight is used to drive charge separation, providing the driving potential for subsequent chemical reactions. Due to the presence of charge transfer (CT) and charge separated (CS) states, the pigments in the RC interact strongly with their protein environment. This sensitivity causes a large dynamic disorder in the RCs due to the protein fluctuations. In this work we report on a first single-molecule spectroscopy study on individual YM210W RC mutants from purple bacterium *Rb. Sphaeroides*. In the single RCs we observe fluorescence (FL) intensity blinking, spec-

tral diffusion and lifetime fluctuations. We obtain both static distributions and dynamic traces, the observed behavior fully agrees with the anticipated dynamic disorder. We find that with increasing FL peak wavelength the spectrum width linearly increases, while the lifetime exponentially decreases. We quantitatively describe the experiments by an excitonic model including charge separation. This model, explaining both bulk and single-RC measurements, shows that the charge separation rate is determined by the fluctuations of the P⁺B⁻ CT state energy, caused by the protein fluctuations.

MO 21.5 Thu 15:15 S HS 001 Biologie

Near field induced speedup of exciton diffusion in light-harvesting arrays — ●ANDREA MATTIONI, FELIPE CAYCEDO-SOLER, SUSANA HUELGA, and MARTIN PLENIO — Institut für Theoretische Physik and Center for Integrated Quantum Science and Technology IQST, Albert-Einstein-Allee 11, Universität Ulm, 89069 Ulm, Germany

The observation of long-range energy propagation along nano-engineered arrays of bacterial antenna complexes [*Nano Lett.*, **2010**, 10 (4), pp 1450–1457] has been recurrently addressed as a result of ballistic, hence, coherent propagation [*J. Phys. Chem. C*, **2012**, 116 (5), pp 3747–3756]. We show that the experimentally determined quantities relevant for these dynamics hinder the formation of large coherent domains and inevitably lead to classical diffusion in these densely packed arrays, which nevertheless benefit from the spectral complexity of single antenna complexes and near field interactions to result in the propagation observed. We show that the packing density bridges the apparent incompatibility between observed energy transfer rates in bacterial photosynthetic membranes and nano-engineered antenna arrays, which together with exciton delocalization across individual antennas and non-equilibrium transport, provides useful design strategies to optimize energy transfer in the presence of typical room temperature conditions.

MO 21.6 Thu 15:30 S HS 001 Biologie

Broadband Time-Resolved Circular Dichroism Spectroscopy of Monolayer MoS₂ — ●HEIKO HILDENBRAND¹, ANDREAS STEINBACHER¹, HOPE BRETSCHER², AKSHAY RAO², and TOBIAS BRIKNER¹ — ¹Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg — ²Department of Physics, Cavendish Laboratory, University of Cambridge, 19 JJ Thompson Avenue, Cambridge, CB3 0HE, UK

Circular dichroism (CD) is a common technique for analyzing chiral samples by their difference in absorption of left and right circularly polarized light. Here we present broadband time-resolved CD spectroscopy which is based on the pump-probe technique paired with a setup capable of mirroring an arbitrary polarization state of an ultra-short laser pulse [1]. Hence, by passing a circularly polarized broadband probe pulse through this setup, we can switch between opposite handedness on a shot-to-shot basis. In combination with a chopping scheme, this allows us to simultaneously acquire data of transient CD and absorption changes.

To demonstrate the capabilities of this approach we selectively excite the K and K' valley of a MoS₂ monolayer on a quartz substrate with circularly polarized femtosecond pulses. Since the valley degree of freedom is only accessible via helicity-sensitive techniques, we investigate the ultrafast valley dynamics by time-resolved CD spectroscopy and complement the results with information obtained via transient absorption spectroscopy of the A and B excitonic bands.

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

MO 21.7 Thu 15:45 S HS 001 Biologie

variational approaches to quantum impurities: from the Fröhlich polaron to the angulon — ●XIANG LI, GIACOMO BIGHIN, ENDERALP YAKABOYLU, and MIKHAIL LEMESHKO — Institute of Science and Technology Austria, Klosterneuburg, Austria

In this contribution we introduce new variational approaches, termed as single phonon expansion, coherent state on top of single phonon excitation, and Pekar diagonalization, to quantum impurities and apply them to the Fröhlich polaron, a quasiparticle formed out of an electron (or other point-like impurity) in a polar medium, and to the angulon, a quasiparticle formed out of a rotating molecule in a bosonic bath. We benchmark these approaches against established theories, evaluating their accuracy as a function of the impurity-bath coupling.

[1] X. Li, G. Bighin, E. Yakaboylu, M. Lemeshko, arXiv: 1810.10302

MO 22: Posters 3: Cluster, Strong Field Physics, and Experimental Techniques

Time: Thursday 16:15–18:15

Location: S Foyer LLM

MO 22.1 Thu 16:15 S Foyer LLM

Angle resolved photoelectron spectra of small copper clusters — ●LUKAS WEISE and BERND V. ISSENDORFF — Physikalisches Institut der Albert-Ludwigs-Universität Freiburg

Angle resolved spectra are important tests for the theoretical description of clusters since they carry more information than the energy spectra alone. The anisotropy of photoelectron spectra for example depends on the angular momentum state.

The cluster anions are produced in a magnetron sputter source and enter a time-of-flight spectrometer for mass measurement and selection. Afterwards electrons are detached by linear polarized laser light and projected onto a MCP detector in a velocity map imaging setup.

Here the results for small copper cluster are presented. Although copper clusters have been studied intensively, there are still undiscovered features of their photoelectron spectra. For example Cu_5^- shows a strong vibrational structure.

MO 22.2 Thu 16:15 S Foyer LLM

Optical spectroscopy of small cluster cations — ●MARKO FÖRSTEL, WOLFGANG SCHEWE, and OTTO DOPFER — TU Berlin, IOAP, Hardenbergstr. 36, 10623 Berlin

Optical spectra of small cationic species are needed to understand the absorption properties of the interstellar medium. They also allow to understand the electronic structure of species relevant for catalysis and material science. Unfortunately, those spectra are not easy to obtain due to intrinsically low target densities.

In this poster presentation we introduce our new tandem quadrupole - reflectron time-of-flight spectrometer coupled to a laser vaporization source for the measurement of optical spectra of cluster cations.^[1] Several improvements allow us to measure optical spectra detailed enough to enable structure determinations via comparisons to TD-DFT based Franck-Condon simulations.^[2]

[1] M. Förstel, B. K. A. Jaeger, W. Schewe, P. H. A. Sporkhorst, O. Dopfer, Improved tandem mass spectrometer coupled to a laser vaporization cluster ion source, *Rev. Sci. Instr.* 2017, 88, 123110.

[2] M. Förstel, W. Schewe, O. Dopfer, Optical spectroscopy of the Au_4^+ cluster: Resolved vibronic structure indicates an unexpected isomer, submitted.

MO 22.3 Thu 16:15 S Foyer LLM

Small silver clusters on porphyrin templates — ●CARL FREDERIC USSLING¹, TOBIAS BISCHOFF¹, ANDRE KNECHT¹, ANDREA MERLI¹, MERLE I. S. RÖHR², POLINA G. LISINetskAYA², JENS PETERSEN², ROLAND MITRIĆ², and THOMAS MÖLLER¹ — ¹Institut für Optik und Atomare Physik, Technische Universität Berlin — ²Institut für Physikalische und Theoretische Chemie, Universität Würzburg

Due to promising applications in nanotechnology, the size- and structure-dependent optical properties of noble metal clusters have been studied for many years. In the smallest size regime, both the cluster geometry and optical properties are strongly influenced by size [1]. Recently, first studies on the collective optical characteristics and interactions between silver clusters arranged in an ordered 2D lattice were published [2]. Furthermore, it has been predicted that porphyrin templates may be used to produce such well defined arrangements, e.g. of cationic Ag_3 clusters [3]. As a first step into the direction of cluster arrays we investigated the possibility to combine cationic Ag_3 clusters with single porphyrins in a collision cell in the gasphase and explored first the optical properties of the produced silver-porphyrin-hybrids in the UV/VIS range.

[1] K. L. Kelly *et. al.*, *J. Phys. Chem. B* **107**, 668 (2003)

[2] P. G. Lisinetskaya *et. al.*, *Phys. Rev. B* **89**, 035433 (2014)

[3] M. Röhr *et. al.*, *J. Phys. Chem. A* **120**, (2016)

MO 22.4 Thu 16:15 S Foyer LLM

Dispersion-controlled docking preference: analyzing isolated dibenzofuran–solvent complexes with IR/UV spectroscopy — DOMINIC BERNHARD¹, ●DOMINIQUE MAUÉ¹, MARIYAM FATIMA^{2,3}, ANJA POBLOTZKI⁵, MARTIN A. SUHM⁵, MELANIE SCHNELL^{2,3,4}, and MARKUS GERHARDS¹ — ¹Physical Chemistry, TU Kaiser-

lautern, Germany — ²Max Planck Institute for the Structure and Dynamics of Matter, Hamburg — ³DESY, Hamburg — ⁴Physical Chemistry, CAU Kiel — ⁵Physical Chemistry, Georg-August Universität Göttingen

The structural preferences within a series of dibenzofuran–solvent complexes has been investigated by electronic, vibrational and rotational spectroscopic methods within supersonic jet experiments. The experimental study is accompanied with a detailed theoretical analysis including dispersion corrected density functional theory, symmetry adapted perturbation theory as well as coupled cluster approaches. The complementary, multi-spectroscopic results of microwave, FTIR and – as presented here – by combined IR/UV spectroscopy reveal a preferred $\text{OH}\cdots\text{O}$ structure for dibenzofuran–water as the smallest complex, whereas for the methanol complex two coexisting $\text{OH}\cdots\text{O}$ and $\text{OH}\cdots\pi$ isomers are revealed. Furthermore, for dibenzofuran–*tert*-butanol as the largest complex within this study, only a π -bound structure is observed. A general trend regarding the binding preference is deduced, which is driven by London dispersion interactions.

MO 22.5 Thu 16:15 S Foyer LLM

Water deprotonation on free calcium-manganese-oxide clusters: Gas Phase Model Systems for the Catalytically Active Center of Photosystem II — ●SANDRA M. LANG, IRENE FLEISCHER, SILVIA MAUTHE, NINA ZIMMERMANN, and THORSTEN M. BERNHARDT — Institute of Surface Chemistry and Catalysis, Ulm University, Albert-Einstein-Allee 47, 89069 Ulm, Germany

The catalytic oxidation of water in plants takes place at an inorganic Mn_4CaO_5 cluster located in photosystem II. To aid the design of new artificial water oxidation catalysts we embark on a novel hierarchical modeling strategy, starting with small clusters and increasing the model system's complexity in a staged, controlled manner.

In the first steps we studied the reactivity of isolated manganese oxide cluster ions, Mn_xO_y^+ , of different size and composition with D_2^{16}O and H_2^{18}O . Gas-phase ion trap experiments and infrared multiple-photon dissociation (IR-MPD) spectroscopy in conjunction with first-principles calculations, revealed the facile water deprotonation and the exchange of the oxygen atoms of the cluster with water oxygen atoms.

In a further step we investigated binary calcium manganese oxide clusters and found that the number of Ca atom is crucial to the water oxidation capabilities of the small $\text{Ca}_{4-x}\text{Mn}_x\text{O}_4^+$ and $\text{Ca}_{5-x}\text{Mn}_x\text{O}_5^+$ clusters. Finally, we started modeling the ligand environment of the manganese-clusters cluster by small acids. First experiments identified propionic acid as the most promising candidate since the smaller acids, formic and acetic acid, easily decompose in the presence of Mn_xO_y^+ .

MO 22.6 Thu 16:15 S Foyer LLM

Strong temperature and size effects in iron-nitrogen interactions — ●ANNIKA STEINER¹, MATTHIAS P. KLEIN¹, SEBASTIAN DILLINGER¹, JENNIFER MOHRBACH¹, PETER B. ARMENTROUT², and GEREON NIEDNER-SCHATTEBURG¹ — ¹Fachbereich Chemie and Forschungszentrum OPTIMAS, Technische Universität Kaiserslautern, 67663 Kaiserslautern, Germany — ²Department of Chemistry, University of Utah, Salt Lake City, Utah 84112, USA

It is a pending challenge to characterize the interaction of N_2 with transition metal surfaces and clusters in detail. For our experiments, we utilized a modified Fourier Transform Ion Cyclotron Resonance Mass Spectrometer (FT-ICR MS). With our tandem cryo trap instrument we investigate N_2 adsorption on Co, Ni, and Rh as well as N_2 and H_2 co-adsorption on Ru_3^+ .

Currently, we investigate Fe_n^+ clusters for reductive nitrogen activation and we conduct temperature dependent studies of N_2 adsorption. We found size and pressure dependent effects, such as extremely slow N_2 adsorption on Fe_{17}^+ . Also, we identified two isomers for the Fe_{18}^+ cluster one of which is unreactive.

Furthermore, we present gas phase IR spectra of N_2 adsorption on isolated cationic Fe_n^+ clusters at cryo temperatures. We find cluster size dependent and adsorbate number dependent effects in the IR spectra. All complexes show single or multiple IR active bands. These bands are significantly red shifted with respect to the IR inactive stretching mode of free N_2 (2359 cm^{-1}).

MO 22.7 Thu 16:15 S Foyer LLM

Ultra-high resolution photoelectron spectroscopy on deeply cold niobium clusters — ●FABIAN BÄR, MORITZ WEIGT, and BERND V. ISSENDORFF — Physikalisches Institut Albert-Ludwigs Universität Freiburg

The properties of deeply cold niobium clusters Nb_4^- to Nb_{35}^- at 3.9 K have been investigated. Therefore, preparatory measurements with platinum ions have been performed, showing that the used magnetic bottle time of flight photoelectron spectrometer has a current resolution of $\Delta E/E = 0.39\%$. This is at least a factor five better than a standard magnetic bottle spectrometer. Striking vibration structures in several photoelectron spectra at cluster temperatures from 3.9 K to 122 K have been found, but so far no evidence for a phase transition involving a superconducting state has been observed. Using an improved setup with a low temperature ion trap and a new spectrometer, vibrational structures of different cluster sizes have been resolved and analysed. In the spectrum of Nb_{26}^- an unexpectedly vibrational transitions have been observed, indicating a cluster geometry with high symmetry. Additionally, the electron affinity of these clusters has been determined at a higher precision.

MO 22.8 Thu 16:15 S Foyer LLM

Cryo kinetics and IR spectroscopy of N_2 and H_2 adsorbed to size selected Rhodium and Tantalum clusters — ●MATTHIAS KLEIN, ANNIKA STEINER, AMELIE EHRHARD, SEBASTIAN DILLINGER, JENNIFER MOHRBACH, and GEREON NIEDNER-SCHATTEBURG — Fachbereich Chemie and Forschungszentrum OPTIMAS, TU Kaiserslautern, Erwin-Schrödinger-Straße 52, 67663 Kaiserslautern

We recorded N_2 adsorption kinetics and InfraRed-PhotoDissociation (IR-PD) spectra of the isolated cluster adsorbate complexes $[\text{Rh}_6(\text{N}_2)_m]^+$, $m=1-12$. In conjunction with extensive DFT modelling, these measurements allow for assignments of the adsorbate arrangement at each adsorption step as well as possible reorganizations of the cluster core structure. By IR-PD spectroscopy combined with DFT modelling we observed a spin quenching with increasing N_2 coverage as well as an adsorption induced relaxation of the cluster structures [1].

Currently, we investigate the N_2 and H_2 adsorption to small size selected Ta_n^+ , $n=2-5$ clusters. Recent studies on the tantalum dimer cation have analyzed the catalytic formation of ammonia from N_2 and H_2 [2]. Our current cryo IR-PD spectroscopy as well as cryo adsorption kinetics may provide for further spectroscopic and kinetic information about reaction precursors and intermediates.

[1] M. P. Klein, A. A. Ehrhard, S. Dillinger, J. Mohrbach, and G. Niedner-Schatteburg, *Top. Catal.* (2018), **61**, 106-118. [2] C. Geng, J. Li, T. Weiske, H. Schwarz, *PNAS* (2018), **115**, 11680-11687.

MO 22.9 Thu 16:15 S Foyer LLM

Investigation of isotope effects in the formation of water clusters — ●REBECCA SCHAF, JOHANNES VIEHMANN, ANDREAS HANS, ARNO EHRESMANN, and ANDRÉ KNIE — Institut für Physik und CIN-SaT, Universität Kassel, Heinrich-Plett-Str. 40, 34132 Kassel, Germany

The production and mass spectrometry of water clusters doped with various molecules is a method suited for the investigation of the behaviour of different molecules in the process of cluster formation. Here, we present an exploration of isotope effects in the generation of clusters. Isotope enrichment is observed in exemplary studies using normal and deuterated water. To quantify the enrichment we calculate isotope distributions and simulate the experimental mass spectroscopy data. Our method is also applicable to cluster of other species, as is exemplarily demonstrated for van der Waals bound neon clusters.

MO 22.10 Thu 16:15 S Foyer LLM

Setup for photoelectron spectroscopy of metal clusters at FLASH — ●FRANKLIN MARTINEZ¹, NORMAN IWE¹, KLARA RASPE¹, MADLEN MÜLLER², JOSEF TIGGESBÄUMKER¹, and KARL-HEINZ MEIWES-BROER¹ — ¹Institut für Physik, Universität Rostock, Albert-Einstein-Str. 23-24, 18059 Rostock — ²Institut für Physik, Universität Greifswald, Felix-Hausdorff-Str. 6, 17489 Greifswald

Photoelectron spectroscopy experiments at a free electron laser, e.g. FLASH in Hamburg, allow studying highly excited nanoscopic particles in the gas phase by means of core-level ionization. In the case of metal clusters, such experiments can study effects like core-hole screening which can indicate size-dependent changes in the binding

character of such species. However, probing small, single-size selected clusters, for example, requires the preparation of a sufficiently high target density in the FEL interaction region. This condition is met by an experimental setup including a high-current cluster source, a radio-frequency ion trap and a dedicated interaction region. A newly designed interaction chamber provides a field-free environment for the operation of field-free electron spectrometers using time-of-flight or electrostatic deflection analyzers. The setup is completed by a high-resolution electron spectrometer designed and built at the group of Prof. v. Issendorff in Freiburg, and can also be supplemented by a wavelength spectrometer for FEL-radiation. The project is funded by the bmbf.

MO 22.11 Thu 16:15 S Foyer LLM

Photoelectron spectroscopy of size-selected clusters at free electron lasers — ●KARIMAN ELSHIMI, PHILIPP ELSÄSSER, FABIAN BÄR, ALEX RUF, and BERND V. ISSENDORFF — Physikalisches Institut Albert-Ludwigs Universität Freiburg

Investigation of small clusters using photoelectron spectroscopy at free electron lasers (FEL) not only will contribute to a better understanding of the electronic structure, and the resulting properties of nanoscale matter, but also will enable deep insights into the many-particle dynamics. Therefore, the aim of this project is to provide a specialized spectrometer system for studying the electronic structure and the dynamics of free mass-selected and temperature-controlled clusters at FEL. This system involves a high-resolution magnetic bottle type photoelectron spectrometer and an ion time-of-flight mass spectrometer. It is combined with an existing high-intensity magnetron cluster source and a low-temperature ion trap for cluster thermalization. The spectrometers are adapted to both the intense cluster beams as well as to the specific parameters imposed by the FEL. The whole machine is designed and built in a collaboration with the group of Prof. Meiwes-Broer in Rostock. One aspect of this development is the design and the construction of the magnetic bottle type photoelectron spectrometer based on experience gained in a similar experiment at FLASH. We present our newly constructed spectrometer including details about its unique features and results of recent measurements.

MO 22.12 Thu 16:15 S Foyer LLM

Strong field ionization probing of $(\text{NO}_2)_2$ intermolecular vibration with ion coincidence imaging — ●LUCIA MERKEL, KATRIN REININGER, JINGMING LONG, MARC J. J. VRACKING, FEDERICO FURCH, CLAUS PETER SCHULZ, and JOCHEN MIKOSCH — Max-Born-Institut, Max-Born-Straße 2A, 12489 Berlin

The intermolecular vibration of the NO_2 dimer has attracted considerable attention in the attosecond community.^[1,2] Collective vibrational excitation of a gas sample can be achieved via impulsive stimulated Raman scattering.

Here we report on a pump-probe study of the $\text{O}_2\text{N-NO}_2$ vibration in which the probing step is conducted via strong field ionization. The sub-8 fs laser pulses used for the experiment are produced by a high repetition rate OPCPA system.^[3] The resulting ions are detected with coincidence velocity mapping, employing three-dimensional (x, y, t) data acquisition with a digital pixelated detector based on the Timepix technology.^[4] To increase the time resolution, the ion time-of-flight is additionally recorded with a high-resolution time-to-digital converter. We present the data analysis, which allows us to characterize the different pathways in which NO_2^+ fragments are produced. Dissociative strong field ionization to the repulsive A_g state is utilized to characterize the vibrational motion in the ground state of $(\text{NO}_2)_2$.

[1] Li et al., *Science*, 322, 5905 (2008).

[2] Spanner et al., *Phys. Rev. A*, 85, 3 (2012).

[3] Furch et al., *Opt. Express*, 24, 19293 (2016).

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

MO 22.13 Thu 16:15 S Foyer LLM

Imprints of the Molecular Electronic Structure in the Photoelectron Spectra of Strong-Field Ionized Triatomic Model Molecules — ●MATTHIAS PAUL — Friedrich-Schiller-Universität Jena, Institut für Physikalische Chemie, Helmholtzweg 4, 07743 Jena

We examine the circular dichroism in the angular distribution (CDAD) of photoelectrons of non-linear triatomic model systems by analyzing their ionization dynamics. For a detailed characterization of the ionization process of our system, we combine quantum dynamical and classical simulation to analyze the evolution of the electronic density during the interaction with circular polarized light. This builds the foundation for an understanding of the complex pattern of the photoelectron mo-

mentum distribution (PEMD) and thus the related CDAD effects. By applying a modified version of the strong-field-approximation (SFA) and the classical trajectory Monte Carlo (CTMC) method, we are able to discriminate the influence of the excited states and the long-range Coulomb interaction on the ionization dynamics, and assign their contributions to the characteristic pattern of the PEMDs. Increasing the internuclear distance or changing the symmetry of the potential strongly affects the three-folded structure in the PEMD, as well as the CDAD. Our analysis allows us to assign these modifications to contribution of excited states.

MO 22.14 Thu 16:15 S Foyer LLM

Strong-field dynamics of singly excited vibronic resonances in the hydrogen molecule — ●GERGANA D. BORISOVA, VEIT STOOS, PAUL BIRK, MAXIMILIAN HARTMANN, TOBIAS HELDT, CHRISTIAN OTT, and THOMAS PFEIFER — Max-Planck-Institut für Kernphysik, Saupfercheckweg 1, 69117 Heidelberg, Deutschland

The effect of strong near-infrared (NIR) laser fields interacting with excited states of the helium atom has been studied with attosecond transient-absorption spectroscopy (ATAS) as well as using electron detection techniques. Looking at molecules, however, not only the electronic but also the nuclear degrees of freedom can be influenced by strong fields. Here, we investigate the dynamics in the presence of a strong NIR laser field in H_2 , the molecular analog of the helium atom. In ATAS spectra we resolve a forest of H_2 vibronic states in the energy region between 13 and 16.5 eV. Comparing to both theoretical [1] and experimental data [1-3] we assign most of the observed resonances to transitions between the ground state of H_2 and higher lying singly excited vibronic states. We observe changes in the XUV absorption spectrum in the presence of moderately strong NIR intensities, $I_{NIR} \sim 10^{12}$ W/cm². This includes the spectral region of the predissociating D-X system with its vibronic excitations, lying energetically above the first ionization threshold of H_2 , and thus coupling to continuum states. How the predissociating character of the D-X transitions is imprinted on the absorption spectrum and the laser control of the initiated dynamics is the main subject of this work. [1] Can. J. Phys. 72, 856 (1994) [2] PRA 94, 023403 (2016) [3] PRA 97, 023401 (2018)

MO 22.15 Thu 16:15 S Foyer LLM

Harmonic spectroscopy of a polymer — ●FRANZISKA FENNEL and STEFAN LOCHBRUNNER — Institute of Physics and Department of Life, Light, and Matter, University of Rostock, Albert-Einstein-Str. 23-25, 18051 Rostock

High-harmonic spectroscopy has developed to a versatile tool to probe structure and ultrafast light-induced processes in complex systems, ranging from multi-electron dynamics in molecules [1] to the electronic band structure of solids [2]. We aim to use harmonic spectroscopy in order to study systems that reside between bulk materials and isolated molecules such as polymers and organic molecular films.

The focus of the presented poster is the characterization of the setup for harmonic generation with MIR pulses. First proof of principle measurements with an organic polymer are presented.

[1] O. Smirnova et al., Nature 460, 972 (2009)

[2] G. Vampa et al., Phys. Rev. Lett. 115, 193603 (2015)

MO 22.16 Thu 16:15 S Foyer LLM

Semiclassical description of high order harmonic generation in H_2^+ — ●FERMÍN RODRÍGUEZ-HERNÁNDEZ¹, FRANK GROSSMANN², and JAN-MICHAEL ROST¹ — ¹Max-Planck-Institut für Physik komplexer Systeme, Nöthnitzer Strasse 38, D-01187 Dresden, Germany — ²Institut für Theoretische Physik, Technische Universität Dresden, D-01062, Germany

High order harmonic generation (HHG) is a key process in intense laser field-matter interaction which has enabled the generation of coherent XUV radiation and attosecond pulses. In this work we investigate HHG for a one-dimensional H_2^+ molecular model using a semiclassical description based on the Herman-Kluk propagator. We do this in the setting of laser assisted electron ion scattering [1], which avoids initial tunneling. We found the semiclassical approach is able to reproduce the major features of the HHG spectrum when (secondary) tunneling is not important. For certain nuclear separations and specific field intensities, structures appear in the HHG spectrum in addition to the ones familiar from atomic HHG. The semiclassical approach and in particular the trajectories facilitate the understanding of those phenomena.

[1] C. Zagoya, C.-H. Goletz, F. Grossmann, and Jan M. Rost, New

J. Phys. 14, 093050 (2012).

MO 22.17 Thu 16:15 S Foyer LLM

Angle-resolved Auger electron spectroscopy resulting from electron-impact ionization of molecules — ●SEBASTIAN FUCHS¹, DANIEL PAUL^{1,2}, TICIA BUHR¹, SÁNDOR RICZ³, and STEFAN SCHIPPERS¹ — ¹I. Physikalisches Institut, Justus-Liebig-Universität Gießen, Germany — ²Max-Planck-Institut für Kernphysik, Heidelberg, Germany — ³Institute for Nuclear Research, Hungarian Academy of Sciences, Debrecen, Hungary

In order to study the angle dependent interactions of polarized electrons as well as circular polarized photons with chiral molecules, an ESA-22-type electron spectrometer [1,2] in combination with an electron gun and focusing optical elements was upgraded and tested. The electron spectrometer is capable of simultaneous energy and angular analysis covering almost the entire polar angular range of emitted electrons. As test experiments, the O K-LL Auger spectra induced by 1.5-keV electron impact were measured using various gas targets (O_2 , CO_2 and N_2O). Auger electrons were detected simultaneously in the polar angular range of 15° to 165° relative to the electron beam direction. The present experimental data are compared with results from earlier experimental studies [3,4,5].

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

[2] L. Ábrók et al., Nucl. Instrum. Methods B 369, 24 (2016).

[3] W. E. Moddeman et al., J. Chem. Phys. 55, 2317 (1971).

[4] A. Hiltunen et al., Nucl. Instrum. Methods B 154, 267 (1999).

[5] W. J. Griffiths et al., J. Phys. B 24, 4187 (1991).

MO 22.18 Thu 16:15 S Foyer LLM

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

Quantum few-body dynamics in atoms and molecules are 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. Excited with ultra-short LASER pulses, these dynamics can be even resolved on attosecond time scale. We designed a new experimental setup to extend this development, enabling 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. Our setup combines 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 22.19 Thu 16:15 S Foyer LLM

Towards Single-Molecule Detection on a Smartphone — ●LARS RICHTER^{1,2}, CAROLIN VIETZ², MAX L. SCHÜTTE², QINGSHAN WEI³, AYDOGAN OZCAN⁴, PHILIP TINNEFELD⁵, and GUILLERMO P. ACUNA^{2,6} — ¹Department of Physics, Humboldt University of Berlin, Berlin, Germany — ²Institute for Physical & Theoretical Chemistry, and BRICS, and LENA, Braunschweig University of Technology, Germany — ³Department of Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, USA — ⁴Electrical & Computer Engineering Department, and Bioengineering Department, and CNSI, and Department of Surgery, University of California, Los Angeles, USA — ⁵Department of Chemistry and Center for NanoScience, Ludwig Maximilian University of Munich, Germany — ⁶Department of Physics, University of Fribourg, Switzerland

Microscopy techniques based on smartphones have seen a rapid development during the last years. Necessitating only a small number of additional camera components, enables smartphone microscopes to detect analytes such as cells, viruses and bacteria.

We demonstrate and test a smartphone microscopy system with single-molecule sensitivity. By employing optical nanoantennas which rely on the plasmonic enhancement with metal nanoparticles, the emitted light intensity per molecule is greatly amplified.

The experimental results show that monochrome camera sensors outperform colour sensors reaching a sensitivity of 10 fluorophores. Furthermore, preliminary results indicate the detection of single fluorescent molecules on a smartphone.

MO 22.20 Thu 16:15 S Foyer LLM

Set-up for systematic studies on liquid flatjet systems

— ●CHRISTINA ZINDEL, CHRISTIAN OZGA, ANDREAS HANS, DANA BLOSS, ANDREAS NEHLS, ARNO EHRESMANN, and ANDRÉ KNIE — Institut für Physik and CINSaT, University of Kassel, Heinrich-Plett-Str. 40, 34132 Kassel, Germany

Within the last years, liquid microjets were commonly used to study fluids and solutions under vacuum conditions. For various spectroscopic applications however, the required sample thickness is limited to a few micrometers down to nanometers, which is barely achievable with common cylindrical microjets. This problem can be solved by

using a so called flatjet system. The collision of two cylindrical jets within their laminar region leads to the formation of liquid sheets, each with an extension in the millimeter range and with a thickness down to a few hundred nanometers. So far, the behavior of these systems is not well understood with regard to different parameters like backing pressure, viscosity and angle of interaction. Here we present a set-up which allows the systematical study of flatjet systems by using a digital light microscope. Additionally, this enables the investigation of its mixing characteristics, i.e. mixing processes within those microjets and liquid sheets.

MO 23: Molecular Theory

Time: Friday 10:30–12:30

Location: S HS 001 Biologie

Invited Talk MO 23.1 Fri 10:30 S HS 001 Biologie
Efficient charge transfer by electron transfer mediated decay mechanism — ●KIRILL GOKHBERG — Theoretical Chemistry, Heidelberg University, Heidelberg, Germany

Charge transfer between atoms and molecules is enabled by several mechanisms. It can proceed due to the coupling to the vibrational degrees of freedom, or via photon emission, in which case it is typically slow. In this talk I will present electron transfer mediated decay (ETMD), a charge transfer process enabled by interatomic electron correlation, which is usually fast. In ETMD charge transfer takes place between singly or multiply ionised atoms embedded in chemical environment and their neighbours, such that the transfer of the electron to the ion is accompanied by the emission of a second electron from the environment to the continuum. Whenever energetically allowed the process is highly efficient. Calculated ETMD lifetimes in rare gas clusters are less than a few picoseconds, while for solvated positive ions they can be as short as few tens of femtoseconds. The theoretical findings were confirmed by recent experiments, which showed the existence of ETMD in salt solutions and mixed rare gas clusters. Importantly, it was demonstrated that this process plays a crucial role in redistributing throughout a larger chemical system a localised positive charge produced by the action of ionising radiation. ETMD was also shown in theory and experimentally to furnish an efficient indirect pathway for producing cold doubly ionised species embedded in He nanodroplets by ionising the host He matrix.

MO 23.2 Fri 11:00 S HS 001 Biologie
Time-dependent Matrix Product States for the Study of Ultrafast Electron Dynamics in Molecules — ●LARS-HENDRIK FRAHM and DANIELA PFANNKUCHE — I. Institut Für Theoretische Physik, Universität Hamburg, Deutschland

Ultrafast dynamics allow to access the complex mechanisms in molecular systems in a very controlled manner. A complete quantum mechanical description, however, is very challenging due to the usually strong correlation of the electrons and the large number of degrees of freedom. The concept of matrix product states (MPS) is able to reduce the effective number of degrees of freedom and to describe strongly correlated systems efficiently. In this work, we present a newly developed ab-initio method using MPS to study such ultrafast electron dynamics in molecules. We show that the method is able to capture the electron dynamics on a full configurational interaction (CI) level up to a few femtoseconds after ionization. We compare results from our MPS method and the full CI method for two distinct molecules, namely the chain of hydrogen atoms and the water molecule. Further, we apply the method to describe ultrafast charge migration in iodoacetylene, for which CI methods are out of range. We find direct agreement between our results, existing experiments, and the literature.

MO 23.3 Fri 11:15 S HS 001 Biologie
An angulon quasiparticle perspective on impulsive molecular alignment in He nanodroplets. — ●IGOR CHEREPANOV, GIACOMO BIGHIN, and MIKHAIL LEMESHKO — IST Austria (Institute of Science and Technology Austria), Am Campus 1, Klosterneuburg, Austria

A quasiparticle picture provides a more straightforward and intuitive understanding of collective many-body phenomena arising in a variety of physical and chemical systems. Moreover, the problems which seem unsolvable within the classical approaches quite often become tractable from the quasiparticle perspective. This is the case for the microscopic dynamics of a single impurity immersed into a superfluid He droplet.

Recently, the first experiments [1] showed that a short laser pulse can induce alignment of molecules dissolved in a He droplet. The rotational wavepacket dynamics herewith cannot be understood in terms of interference of the rigid rotor states due to the strong interactions with surrounding helium. Here we develop a dynamical theory of angulons [2] – quasiparticles consisting of a rotating impurity dressed by a field of surrounding bath excitations (phonons). We demonstrate that the superfluid helium environment strictly limits the number of molecular states which can survive for a long time. Our theoretical framework allows to compute the change of the angular momentum belonging to the molecule and the helium bath in time. It opens up a possibility to have a look at the molecular alignment experiments from the point of view of redistribution of angular momentum. [1] D. Pantleher et al., Phys. Rev. Lett. 110, 093002 (2013) [2] R. Schmidt, M. Lemeshko, Phys. Rev. Lett. 114, 203001 (2015)

MO 23.4 Fri 11:30 S HS 001 Biologie
The multiconfigurational Ehrenfest method for the relaxation of excited molecules in the condensed phase — ●MARTIN PESCHEL¹, MATTEO BONFANTI², DAVID PICCONI², IRENE BURGHARDT², and REGINA DE VIVIE-RIEDLE¹ — ¹Ludwig-Maximilians-University Munich — ²Goethe-University Frankfurt

Coherences and correlation with the environment can affect the relaxation behaviour of excited molecules in the condensed phase. Multiconfigurational methods enable us to systematically study these effects. In the multiconfigurational Ehrenfest (MCE) method the amount of correlation described is tuned by successively including more and more configurations, thus smoothly transitioning from uncorrelated to fully correlated dynamics [1]. MCE so far has mainly been used to study quantum subsystems with only a small number of states, but it can readily be extended to allow a grid-based description of a quantum subsystem in the condensed phase.

We apply this method to a description of excited iodine in a krypton matrix with a look at dissipation, decoherence and the autocorrelation function [2]. We then advance to the more involved example of uracil in water at room temperature. Here we combine MCE with our previously developed coupled quantum dynamics/molecular dynamics approach to fully capture the solute-environment interaction during the relaxation process.

[1] T. Ma *et al.*, *J. Chem. Phys.*, **149** (2018), accepted manuscript.

[2] D. Picconi *et al.*, submitted.

MO 23.5 Fri 11:45 S HS 001 Biologie
Non-Markovian quantum dynamics of vibronic systems with controlled factorization of the environment — ●ALEJANDRO D. SOMOZA, OLIVER MARTY, JAEMIN LIM, SUSANA F. HUELGA, and MARTIN B. PLENIO — Institut für Theoretische Physik and IQST, Universität Ulm, Ulm, Germany

Charge and energy transfer in biological and organic materials are often characterized by the coupling of excitations to high-frequency underdamped vibrations and a slow background accounting for solvent reorganization effects. The simulation of many interacting chromophores, strongly coupled to intramolecular modes of vibration and embedded in a dissipative environment requires a substantial computational effort. Numerically exact methods are typically limited to just a few sites and, often, severe approximations with poor error control are required in order to address large systems. In this work, we devise an algorithm that partially eliminates weak correlations among oscillators, while preserving as much as possible the entanglement between

the electronic system and the vibrational environment. We exploit the memory-efficient representation of matrix product operators (MPOs) to rewrite the bosonic states in a form that parametrically interpolates between fully factorized oscillators and an exact description of the vibrational environment where no correlations are discarded. A straight forward measure of the error is obtained and the factorization can be adaptively controlled to keep the error below a well-defined bound.

MO 23.6 Fri 12:00 S HS 001 Biologie

Ab Initio Simulations of P-Compounds at Mineral Surfaces

— ●PRASANTH BABU GANTA, ASHOUR AHMED, and OLIVER KÜHN — Institute of Physics, University of Rostock, D-18059 Rostock, Germany Phosphorus (P) plays an important role in the environmental nutrient cycle. Facing the projected peak P scenario, substantial research work have been triggered for efficient use of P resources. One major factor playing a role in the P immobilization is the strong interaction of phosphates to soil mineral surfaces (Fe-, Al- oxyhydroxides). We have studied binding of two abundant phosphates (inositol-hexa phosphate (IHP), glycerolphosphate (GP)) at two different mineral surfaces (goethite (FeOOH) and diaspore (AlOOH)). Here, water as an aqueous solution in soil was involved around each phosphate mineral model. Here, all models are treated by DFT using PBC. Due to size of our models, QM/MM calculations have been performed to have good accuracy with less computational time. Here, the top two layers of mineral surface, phosphate, and the surrounding water molecules are described at QM level. During MD simulations, different binding motifs including monodentate and bidentate are observed between the phosphates and mineral surfaces. Moreover, protons transfer from phosphates to the mineral surfaces as well as to the surrounding water molecules.

More details will be given in the presentation.

MO 23.7 Fri 12:15 S HS 001 Biologie

Low temperature HD + *ortho/para*-H₂ and HD+H inelastic scattering of astrophysical interest — ●RENAT SULTANOV — 201 W. University Blvd., Department of Mathematics and Engineering, Odessa College, Wood Building of Math and Science (WOOD) Room 213, Odessa, TX 79764

State-selected total cross sections and thermal rate coefficients are computed for the 4-atomic HD + H₂ and 3-atomic HD+H rotational energy transfer collisions at low temperatures (T) of astrophysical interest: 5K < T < 500K. Together with the H₂ + H₂ and H₂ + H collisions, the scattering processes with the participation of the HD molecule (D is deuterium) are of significant importance in the astrophysics of the early Universe, in terms of the modeling of pre-galactic clouds and planetary atmospheres [1]. In the 4-atomic case a precise H₂-H₂ potential energy surface (PES) from paper [2] has been modified and used. The modification procedure was developed in a recent paper [3]. A quantum-mechanical dynamical approach is applied in the current calculation. A comparison between our new results for HD + H₂ and previous calculations [3,4,5] will be presented. The HD+H non-reactive scattering cross sections will also be presented and discussed.

1. A. Dalgarno, R. McCray, Ann. Rev. Astron. Astroph. 10, 375 (1972).
2. K. Patkowski et al., J. Chem. Phys. 129, 094304 (2008).
3. R.A. Sultanov et al., J. Phys. B49 015203 (2016).
4. D. R. Flower, J. Phys. B32, 1755 (1999).
5. J. Schaefer, Astron. Astrophys. Suppl. Ser. 85, 1101 (1990).

MO 24: Large and Reactive Systems

Time: Friday 10:30–12:30

Location: S HS 002 Biologie

MO 24.1 Fri 10:30 S HS 002 Biologie

Effectiveness of Dye Sensitized Solar Cells (DSSCs) based on Cu-doped TiO₂ photoanodes. — ●SARA CHAHID — SCEM research group, Department of Physical Chemistry, Faculty of Sciences, University of Cádiz, 11510, Puerto Real (Cádiz), Spain.

In this research, Cu-doped TiO₂ nanostructures with different doping contents from 0 to 10.0% (mole fraction) were synthesized through hydrolysis at low temperature. The as-prepared Cu-doped TiO₂ nanostructures was characterized with several techniques, X-ray diffraction (XRD) and Raman spectroscopy were used to study the morphology and structure of the nanoparticles, which confirmed the crystalline anatase tetragonal structure. The UV-Vis Spectroscopy analysis was found that incorporation of Cu²⁺ into titanium affects the band gap of TiO₂ and extending his activity towards visible sunlight region. Scanning Electron Microscopic (SEM) analysis confirming the Cu content is incorporated into TiO₂ lattice affecting efficiency of doped samples. Further, the active specific surface area of the system was investigated employing Brunauer-Emmet-Teller (BET) measurement. Then the Dye-sensitized solar cells (DSSCs) based on Cu-doped TiO₂ photoanodes were fabricated and investigated with chemically absorbed Ruthenium N3 dye electrode under light illumination with standard solar simulator (AM 1.5G, 100mW/cm²). Results demonstrated that the 1.0% Cu-doped TiO₂ sample annealed at 773K for 60 minutes exhibited the best photovoltaic performance of open circuit voltage (V_{oc} = 957.5 mV), short circuit current density (J_{sc} = 0.795 mAcm⁻²), and the cell efficiency was reached (η = 4.524%), which consists 50% higher than the un-doped cell. This study may open up more investigated works applying Cu doped TiO₂ in photovoltaic fields.

MO 24.2 Fri 10:45 S HS 002 Biologie

Synthesis of cubic tin sulfide nanocrystals: growth mechanism unfolded by organic ligands adsorption — ●ELAD SEGEV^{1,2}, RAN EITAN ABUTBUL^{1,2}, URI ARGAMAN¹, YUVAL GOLAN^{1,2}, and GUY MAKOV^{1,2} — ¹Department of Materials Engineering, Ben-Gurion University of the Negev, Beer-Sheva 84105, Israel — ²Ilse Katz institute for Nanoscale science and Technology, Ben-Gurion University of the Negev, Beer-Sheva 84105m Israel

Novel metastable cubic phase was recently discovered in tin monosulfide and monoselenide systems. Surface energy calculations and experimental studies indicate that this cubic phase is stabilized by specific

ligands adsorption on the surface. In this work, it is shown experimentally that HCl molecule, which incorporated to the reaction medium as Oleylammonium chloride (OACl) salt, stabilized those novel phases. The ab-initio computations with adsorbed ligands show lower surface energies for the cubic phase and for the orthorhombic phase than for the pristine surfaces. It is shown that Cl bonds are replacing the missing Sn-S bonds on the surface in the cubic structure. We show that high ligand concentration reaching a full surface coverage enables the cubic nanoparticles to stabilize while for the same concentration the orthorhombic nanoparticles collapse.

MO 24.3 Fri 11:00 S HS 002 Biologie

Fate of inorganic and organic P-compounds: new insights from quantum-chemical modelling — ●ASHOUR AHMED and OLIVER KÜHN — Institute of Physics, University of Rostock, Rostock, Germany

Facing the projected peak phosphorus (P) scenario, substantial research activities have been triggered to improve our knowledge towards a more efficient and sustainable use of P resources. One major factor playing a role in the P immobilization is its strong interaction with soil mineral surfaces and especially with Fe- and Al-oxides. A systematic molecular-level picture of the P binding mechanism at mineral surfaces is still lacking. Therefore, our main target is to explore the molecular binding mechanism for the P adsorption at mineral surfaces in the presence of water. The current presentation is focusing on simulation the binding of different organic and inorganic P compounds with the goethite (α -FeOOH) and its isomorphous (diaspore, α -AlOOH) mineral surfaces. Here, periodic DFT MD simulations are applied to explore possible binding mechanisms for these P compounds at different surface planes. The simulation results indicated to covalent bond formation between P and the mineral surfaces with several binding motifs. These interactions are accompanied by formation of H-bonds, proton transfer, and water dissociation at the mineral surface. More results will be introduced through our presentation at the conference. References 1. Kruse et al., Journal of Plant Nutrition and Soil Science 178, 43 (2015) 2. Ahmed et al., Physical Chemistry Chemical Physics 20, 1531 (2018)

MO 24.4 Fri 11:15 S HS 002 Biologie

Transient absorption spectroscopy of nanodiamonds in water: direct observation of solvated electrons — ●CHRISTOPH

MERSCHJANN¹, FRANZISKA BUCHNER¹, BENJAMIN KIENDL², AMÉLIE VENEROSY³, HUGUES GIRARD³, JEAN-CHARLES ARNAULT³, EMINA HADZIFEJZOVIC⁴, JOHN FOORD⁴, ANKE KRUEGER², and TRISTAN PETIT¹ — ¹Helmholtz-Zentrum Berlin, Germany — ²Universität Würzburg, Germany — ³CEA-LIST, Saclay, France — ⁴University of Oxford, United Kingdom

Nanodiamonds (ND) are promising candidates for photocatalytic transformation of CO₂ to CO and organic reduction products like methanol or formic acid, as they release solvated electrons to the aqueous solution upon UV illumination. However, the nature of the electron emission process and its related dynamics are still unknown.

We investigate the ultrafast dynamics of this process using femtosecond transient absorption spectroscopy with DUV (225 nm) pump and VIS supercontinuum probe pulses. While the recombination of solvated electrons is governed by long-lived (> 2 ns) diffusion processes, NDs of different surface termination (-H, -OH, -COOH) show characteristic features in the sub-picosecond regime. We will discuss the impact of these surface terminations on the dynamics of solvated electrons, and thus on the photocatalytic performance in water. We expect that our results will support the design of efficient metal-free photocatalysts for CO₂ conversion.

Financial support by the European Union's Horizon 2020 Program (Grant Agreement no. 665085, "DIACAT") is gratefully acknowledged.

MO 24.5 Fri 11:30 S HS 002 Biologie

Joining Microfluidics with Infrared Photodissociation: Shedding Light on ortho-Quinone Methides, a Highly Reactive and Transient Intermediate — ●MARTIN MAYER, MAX GRELLMANN, and KNUT R. ASMIS — Wilhelm-Ostwald-Institut für Physikalische und Theoretische Chemie, Universität Leipzig, Linnéstrasse 2, D-04103 Leipzig, Germany

Chemical microreactors, such as microfluidic chips, are revolutionizing the way we can study chemical reactions by making time scales available that were not reachable with conventional techniques. Here, we combine microfluidic chips with the structure determining power of infrared photodissociation (IRPD) spectroscopy to shed light on the in-situ formation of ortho-quinone methides (o-QM). Those highly reactive, transient and therefore not isolatable intermediates occur in innumerable natural processes and have a huge potential in organic synthesis, especially regarding stereoselective reactions. The ephemerality of o-QMs often prevents their investigation by conventional analytical methods. By coupling microfluidics with IRPD spectroscopy, we are not only able to characterize the structures, but also determine E/Z ratios of o-QMs which are produced in-situ on chip. This information is given by the analysis of the IR fingerprint regions of the short-lived species. Control over stereoselectivity is achieved by introducing Lewis acidic alkali metal ions into the reactions and monitoring stereoisomer-selective IR absorption bands which reflect the resulting E/Z ratio. With this multidimensional approach we are able to gain a deeper understanding and control over the formation of elusive o-QMs.

MO 24.6 Fri 11:45 S HS 002 Biologie

Infrared Emission from Thermally Excited Strongly Coupled Vibrational Transitions — ●MARCUS SEIDEL, ANOOP THOMAS, THIBAUT CHERVY, KALAIVANAN NAGARAJAN, ELOISE DEVAUX, CYRILIAQUE GENET, and THOMAS W. EBBESEN — ISIS & icFRC, University of Strasbourg, CNRS, 67000 Strasbourg, France

The strong coupling of vibrational transitions to microcavity resonances has shown a decisive impact on chemical reactivity and like-

wise presents an exciting platform for studying quantum effects related to the light-matter hybridized quasi-particles, called vibro-polaritons [1,2]. Recently, first data was obtained from vibro-polariton thermal emission [3]. Here, we significantly extend this initial work. We present temperature and cavity tuning dependent emission measurements from strongly coupled liquids, namely diethyl sebacate and tetrachloroethylene. This results in better cavity tunability and an increased range of polariton excitation densities. Furthermore, we complement the experimental method by normal incidence reflection measurements and by employing microcavities with dielectric mirrors. The performed experiments lead to a reinterpretation of the previously reported results. In particular, we show that the investigated vibro-polaritonic states are thermalized and that polariton-polariton interactions cannot be readily extracted from the emission data. Our results are important for pioneering vibro-polariton interactions which are crucial for condensation of the quasi-particles. References: [1] T. W. Ebbesen, *Acc. Chem. Res.* 49, 2403 (2016). [2] D. S. Dovzhenko et al., *Nanoscale* 10, 3589 (2018). [3] T. Chervy et al., *ACS Photon.* 5, 217 (2018).

MO 24.7 Fri 12:00 S HS 002 Biologie

Can you hear an axon growing? — ●FREDERIC FOLZ¹, LUKAS WETTMANN¹, GIOVANNA MORIGI¹, and KARSTEN KRUSE² — ¹Theoretische Physik, Universität des Saarlandes, 66041 Saarbrücken, Germany — ²NCCR Chemical Biology, Departments of Biochemistry and Theoretical Physics, University of Geneva, 1211 Geneva, Switzerland

Axons are linear structures of nerve cells that can range from a few tens of micrometers up to meters in length. In addition to external cues, the length of an axon is also regulated by unknown internal mechanisms. Molecular motors have been suggested to generate oscillations with an axon-length dependent frequency that could be used to measure an axon's extension. Here, we present a mechanism for determining the axon length that couples the mechanical properties of an axon to the spectral decomposition of the oscillatory signal.

MO 24.8 Fri 12:15 S HS 002 Biologie

Diagrammatic Monte Carlo approach to angular momentum in quantum many-body systems — ●GIACOMO BIGHIN¹, TIMUR TSCHERBUL², and MIKHAIL LEMESHKO¹ — ¹IST Austria (Institute of Science and Technology Austria), Am Campus 1, 3400 Klosterneuburg, Austria — ²Department of Physics, University of Nevada, Reno, NV, 89557, USA

We introduce a Diagrammatic Monte Carlo (DiagMC) approach to molecular impurities, possessing rotational degrees of freedom [1]. The technique is based on a diagrammatic expansion [2] that merges the usual Feynman diagrams with the angular momentum diagrams known from atomic and nuclear structure theory, thereby incorporating the non-Abelian algebra inherent to quantum rotations. Due to the peculiar way in which angular momenta couple, the configuration space is larger with respect to most DiagMC applications, and a new class of updates is needed in order to span it completely.

We exemplify the technique by obtaining an all-coupling solution of the angulon model - essentially a molecular impurity in a quantum many-body environment - showing that our approach correctly recovers the strong-coupling limit. However, the technique is general and can be applied to a broad variety of systems possessing angular momentum degrees of freedom, thereby establishing a far-reaching connection between DiagMC techniques and molecular simulations.

[1] G. Bighin, T. V. Tscherbul, and M. Lemeshko, *Phys. Rev. Lett.* 121, 165301 (2018). [2] G. Bighin and M. Lemeshko, *Phys. Rev. B* 96, 419 (2017).